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U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF CHEMISTRY—BULLETIN No. 90.

H. W. WILEY, Chief of Bureau.

PROCEEDINGS

OF THE

TWENTY-FIRST ANNUAL CONVENTION

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

HELD AT

ST. LOUIS, MO., SEPTEMBER 26, 27, AND 28, 1904.

EDITED BY

HARVEY W. WILEY,

SECRETARY OF THE ASSOCIATION.

WASHINGTON:

GOVERNMENT PRINTING OFFICE.

1905.

LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Chemistry,
Washington, D. C., February 2, 1905.

Sir: I have the honor to transmit herewith the manuscript of the proceedings of the twenty-first annual meeting of the Association of Official Agricultural Chemists, with the request that it be published as Bulletin No. 90 of this Bureau.

Respectfully,

H. W. Wiley,
Chief of the Bureau of Chemistry and Secretary of the Association of Official Agricultural Chemists.

Hon. James Wilson,
Secretary of Agriculture.

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PROCEEDINGS OF THE TWENTY-FIRST ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

FIRST DAY.

MONDAY—MORNING SESSION.

The twenty-first annual convention of the Association of Official Agricultural Chemists was held in the Hall of Congresses, Louisiana Purchase Exposition, St. Louis, Mo. In the absence of the president and vice-president the meeting was called to order at 10 o'clock on the morning of September 26, 1904, by the secretary, and Mr. W. A. Withers, of Raleigh, N. C., was elected president pro tem.

The following members and visitors were in attendance during the sessions of the convention:

MEMBERS AND VISITORS PRESENT.

Allen, W. M., North Carolina Department of Agriculture, Raleigh, N. C.

Bailey, M., jr., Agricultural Experiment Station, New Haven, Conn.
Barnard, H. E., State Laboratory of Hygiene, Concord, N. H.
Beal, W. H., U. S. Department of Agriculture, Washington, D. C.
Berkeley, W. N., Superior Board of Health, San Juan, P. R.
Bernays, Walter, City Chemist, St. Louis, Mo.
Bigelow, W. D., U. S. Department of Agriculture, Washington, D. C.
Bizzell, J. A., Cornell University Experiment Station, Ithaca, N. Y.
Browne, C. A., jr., Agricultural Experiment Station, New Orleans, La.
Burd, J. S., Agricultural Experiment Station, Moscow, Idaho.
Burnet, W. C., Mallinckrodt Chemical Co., St. Louis, Mo.

Carpenter, F. B., Virginia-Carolina Chemical Company, Richmond, Va.
Carroll, J. S., German Kali Works, Atlanta, Ga.
Caspari, C. E., St. Louis College of Pharmacy, St. Louis, Mo.
Claflin, Alan A., Littleton, Mass.
Cluff, C. B., American Cotton Oil Company, St. Louis, Mo.

Davidson, R. J., Agricultural Experiment Station, Blacksburg, Va.
Doyle, Aida M., U. S. Department of Agriculture, Washington, D. C.

Eaton, Edward N., State Analyst, Chicago, Ill.

Fischer, Richard, State Chemist, Madison, Wis.
Fraps, Geo. S., Associate Chemist, College Station, Tex.

Graessner, P. A., Director Potash Works, Stassfurt, Leopoldshall, Germany.

Halligan, J. E., Agricultural Experiment Station, New Orleans, La.
Harms, Herman, State Chemist, Salt Lake City, Utah.
Headden, Wm. P., Agricultural Experiment Station, Fort Collins, Colo.
Hobbs, P. L., Dairy and Food Commission, Cleveland, Ohio.
Holland, E. B., Hatch Experiment Station, Amherst, Mass.
Hopkins, C. G., Agricultural Experiment Station, Urbana, Ill.
Hortvet, Julius, State Chemist, St. Paul, Minn.
Howard, B. J., U. S. Department of Agriculture, Washington, D. C.
Huston, H. A., German Kali Works, St. Louis, Mo.

Jones, W. J., Chief Deputy State Chemist, Lafayette, Ind.

Kebler, Lyman F., U. S. Department of Agriculture, Washington, D. C.
Kerr, G. A., Acme Bark Extract Company, Damascus, Va.
Knisely, A. L., Agricultural Experiment Station, Corvallis, Oreg.

La Bach, J. O., Kentucky Pure Food Control, Lexington, Ky.
Lachman, Henry, San Francisco, Cal.
Ladd, E. F., Agricultural Experiment Station, Fargo, N. Dak.
Langley, Ralph W., Old City Hall, St. Louis, Mo.
Leach, A. E., State Board of Health, Boston, Mass.
Leavette, Geo. G., 134 Kinzie Street, Chicago, Ill.
Le Clerc, J. A., U. S. Department of Agriculture, Washington, D. C.

McCarty, E. R., Acme Bark Extract Company, Damascus, Va.
McDonnell, C. C., Agricultural Experiment Station, Clemson College, S. C.
McKeefe, E. P., State Department of Agriculture, Albany, N. Y.
Magruder, E. W., Department of Agriculture, Richmond, Va.
Mardick, J. R., Wm. V. Mosser & Co., Du Bois, Pa.
Martin, W. C., Agricultural Experiment Station, College Station, Tex.
Moore, C. C., U. S. Department of Agriculture, Washington, D. C.
Myers, G. I., 310 East Fifteenth street, Kansas City, Mo.

Newborne, R. G., Kentucky Tobacco Product Company, Louisville, Ky.
Nichols, M. F., Nichols Laboratory, Grand Rapids, Mich.
Norris, C. W., 612 Commerce Street, Milwaukee, Wis.
Norton, J. H., Station Chemist, Fayetteville, Ark.

Olson, G. A., Agricultural Experiment Station, Madison, Wis.

Parkinson, Nellie, U. S. Department of Agriculture, Washington, D. C.
Pate, W. F., Agricultural Experiment Station, Urbana, Ill.
Patten, A. J., Agricultural Experiment Station, Geneva, N. Y.
Pettit, J. H., Agricultural College, Urbana, Ill.
Pierce, Anne L., U. S. Department of Agriculture, Washington, D. C.

Ray, E. O., 108 Lasalle Street, Chicago, Ill.
Reed, H. C., Stamford Manufacturing Company, Stamford, Conn.
Ross, B. B., State Chemist, Auburn, Ala.

Schaub, I. O., Agricultural Experiment Station, Urbana, Ill.
Scherffius, W. H., Agricultural Experiment Station, Lexington, Ky.
Scoville, M. A., Agricultural Experiment Station, Lexington, Ky.
Sessums, I. D., Agricultural College, Miss.
Small, F. H., 722 Pleasant street, Worcester, Mass.
Smith, L. H., Agricultural Experiment Station, Urbana, Ill.
Snyder, H., Agricultural Experiment Station, St. Anthony Park, Minn.
Stark, W., Agricultural College, Miss.

Stewart, R., Agricultural Experiment Station, Logan, Utah.
Street, J. P., Agricultural Experiment Station, New Brunswick, N. J.

Taylor, E. R., Penn Yan, N. Y.
Teas, W. H., Elk and Penn Tanning Companies, Ridgway, Pa.
Thatcher, R. W., Agricultural Experiment Station, Pullman, Wash.

Van Slyke, L. L., Agricultural Experiment Station, Geneva, N. Y.
Veitch, F. P., U. S. Department of Agriculture, Washington, D. C.
Von Herff, B., German Kali Works, New York, N. Y.

Warner, H. J., U. S. Department of Agriculture, Washington, D. C.
Weber, F. C., U. S. Department of Agriculture, Washington, D. C.
Wheeler, H. J., Agricultural Experiment Station, Kingston, R. I.
Wiley, H. W., U. S. Department of Agriculture, Washington, D. C.
Williams, C. B., North Carolina Department of Agriculture, Raleigh, N. C.
Williams, J. R., American Car Company, St. Louis, Mo.
Withers, W. A., Agricultural Experiment Station, Raleigh, N. C.
Wilson, H. F., Buena Vista, Va.
Worthen, E. L., Illinois Soil Survey Party, Champaign, Ill.

The order of business was as follows:

ORDER OF BUSINESS.

Appointment of committees.
The president's letter.
Reports of the referees:

1. Sugar.
2. Tannin.
3. Insecticides.
4. Foods and feeding stuffs.
5. Food adulteration.
6. Dairy products.
7. Soils.
8. Ash.
9. Potash.
10. Determination of nitrogen.
11. Separation of nitrogenous bodies.
12. Phosphoric acid.
13. Medicinal plants and drugs.

Reports of the special committees:

1. Food standards.
2. Fertilizer legislation.
3. Testing chemical reagents.
4. Committees A, B, and C on recommendations of referees.

APPOINTMENT OF COMMITTEES.

The presiding officer proceeded at once to the appointment of committees A, B, and C on recommendations of referees:

Committee A (phosphoric acid, potash, nitrogen, soils, ash, and insecticides): Messrs. Williams, Hopkins, Thatcher, and Avery. (Later amended by the addition of the name of Mr. J. P. Street.)

Committee B (dairy products, foods, and feeding stuffs, sugar, and tannin): Messrs. Browne, Veitch, Robison, and Crampton. (Later amended to include Messrs. Ladd, Van Slyke, and Teas.)

Committee C (food adulteration): Messrs. Bigelow, Barnard, Grindley, and Allen. (Later amended by the addition of the name of Mr. Leach.)

The following letter of greeting from President Jaffa was read by the secretary in lieu of the usual presidential address:

PRESIDENT'S LETTER.

BERKELEY, CAL., *September 22, 1904.*

To the members of the Association of Official Agricultural Chemists:

GENTLEMEN: It is greatly to my regret that I find it impossible to be present at your meeting this year and take part in the deliberations. I am especially sorry that I am unable to address you in person and express to you my thanks for the honor conferred upon me at your last meeting, when you elected me your president. Allow me to express to you in this manner and in this poor way my deep appreciation of the honor, and the unmerited compliment which it implied.

My regret at my enforced absence is all personal, for I know that your worthy vice-president will fill the president's chair and discharge the duties of the office with far more grace and skill than could the president himself.

Permit me to extend to you my heartiest congratulations upon this your twenty-first anniversary. You have attained your majority, and the world has a right to expect great things of you. You must now bend every effort toward fulfilling the promise of your early life. In the coming years of your maturity you must not be satisfied to merely retain the prominent and dignified position which you have already won for yourself. You must endeavor to do such good and thorough work as will make you a power in the scientific movement of the Old as well as the New World.

Wishing you a most profitable and successful session, I am,

Yours, very sincerely, M. E. JAFFA.

The report on sugar was called for, and in the absence of the referee the associate referee on special analytical methods, Mr. Browne, presented the following reports:

REPORT ON SUGAR.

By L. S. MUNSON, *Referee.*

The work on sugar during the past year has been in part a continuation of the lines begun in previous years, but has consisted largely in the investigation of new problems in connection with special sugar methods and methods for molasses analysis.

No associate referee on chemical methods was appointed at the last meeting, it being understood that the referee should continue this line of work. But little analytical work has been done on reducing sugars during the year and the limited results obtained do not warrant any report at this time. The effort has been made to secure some definite cooperation of this association with the committee of the International Commission for Unifying Methods of Sugar Analysis, having under consideration the revision of reducing-sugar methods. The referee communicated with Doctor Wiechmann, the American member of this committee, who in turn referred the matter to Doctor Herzfeld, the chairman of the committee. Both Doctor

Herzfeld and Doctor Wiechmann expressed themselves as desiring to secure the cooperation of this association in the establishment of satisfactory reducing-sugar methods. In view of this fact, the referee has taken the liberty of stating the position of this association and assuring the committee of our support in the effort to secure uniform sugar methods.

The international commission meets in Rome in 1906, at which time this matter will be taken up for consideration, and it is the opinion of the referee that much of the time of the sugar referee and his associates may well be spent during the coming two years in work on this one problem. The reducing-sugar methods of our association are far from satisfactory, and no opportunity should be lost to secure more satisfactory and, at the same time, uniform methods.

Mr. C. A. Browne, associate referee on special analytical methods, has studied methods of determining dextrose and levulose in cane juices and products derived therefrom and has made an investigation of carbohydrates other than sugars, which are present in sugar-house products. The work on special analytical methods in the past has been largely in connection with the beet-sugar industry, while the work this year has been upon cane products, although it is important to both the beet and cane sugar industries. Mr. Browne will present a paper giving the results of his work.

At the last meeting for the first time an associate referee on molasses analysis was appointed. Mr. H. E. Sawyer took up this work and has continued it along the line suggested by his paper on "Molasses and Molasses Analysis" read before the association last year. A brief report of Mr. Sawyer's work is presented in a separate paper.

RECOMMENDATIONS.

The sugar referee and his associates offer the following recommendations for future work.

(1) Chemical methods:

(*a*) That the sugar referee and his associate on chemical methods devote as much time as seems desirable, during the coming year, to cooperation with the committee of the international commission for unifying methods of sugar analysis, having in charge the revision of reducing-sugar methods, for the purpose of obtaining more satisfactory and more uniform methods of determining reducing sugars.

(2) Special analytical methods:

(*a*) That the methods for the determination of levulose and dextrose in the presence of sucrose be given further trial.

(*b*) That the study of methods for the identification and analysis of the vegetable gums be continued.

(*c*) That some effort be made toward perfecting methods for the determination of caramel and the other organic solids which accompany sugar in cane and beet products.

(3) Molasses analysis:

(*a*) That the association consider the adoption of the neutral oxalate of potassium in place of sodium carbonate as a precipitant for lead from clarified sugar solutions which are to be tested for reducing sugars. It has been known for several years that an excess of sodium carbonate redissolves a portion of the lead precipitate in the presence of invert sugar. It has been found by the associate referee that potassium oxalate does not behave in this objectionable manner, and, so far as he has been able to ascertain, there is no drawback to its use.

It is not recommended that the present method be changed this year, but it is suggested that the referee on sugar for the next year be requested to test this new precipitant.

(*b*) That the referee on sugar, or one of his associates, be requested to submit to collaborative test next year the methods of molasses analysis outlined at the meeting in 1903.[a]

REPORT ON SPECIAL ANALYTICAL METHODS OF SUGAR ANALYSIS.

By C. A. Browne, jr., *Associate Referee on Sugar.*

I. The Determination of Levulose in the Presence of Dextrose and Sucrose.

A number of different methods have been proposed from time to time for the determination of levulose in the presence of dextrose and sucrose, among which may be mentioned the following:

1. *Sieben's method.*—This method is based upon the destructive action of hot hydrochloric acid upon levulose, the dextrose remaining comparatively unaffected. The method has been studied by Wiechmann, whose work discloses several objections to the process. The main difficulties consist in an imperfect destruction of the levulose and a partial destruction of the other sugars.

2. *Winter's method.*—Winter used this method in Java in the study of sugar-cane products. The method is based upon the precipitation of the reducing sugars by means of ammoniacal lead acetate. After filtration, the lead precipitate is decomposed first with carbon dioxid, which breaks up the lead dextrosate, and then, after filtering, with hydrogen sulphid, which decomposes the lead levulose compound. The inherent objections to this method are the large amount of time and trouble involved in the work of manipulation and the uncertainty of securing perfect separations.

3. *Wiley's optical method.*—This method, as developed by Wiley, is based upon the difference in polarization of levulose at widely different temperatures, the specific rotation of the associated sugars not being sensibly affected. The method is a rapid one and gives good results. Important precautions are required in the work of polarization, for which specially devised tubes have been constructed.

4. *A combination method.*—Knowing the polarization, sucrose, and copper-reducing power of the mixture, the percentages of both levulose and dextrose admit of calculation. This method has been employed by Stein, Pellet, Prinsen-Geerligs, and others, and may be said to be the method generally in use at present.

During the past year a large number of determinations of the different sugars in sugar-cane products has been made at the Louisiana sugar experiment station. Owing to the pressure of the work it was necessary to select methods which, while giving promise of accuracy, were easy of execution. A determination of levulose in the various products by each of the four methods above outlined could not be attempted, and the work was therefore limited to a comparison of the optical and combination methods.

DESCRIPTION OF METHODS.

Optical method.—The method of procedure is essentially that given by Wiley.[b] The polarizations were carried out in a specially constructed 200 mm metal tube. In making the readings at very low temperatures, especially in summer, the ends of the tubes had to be protected against the deposition of moisture and this was done by means of extra caps. Owing to the dilution resulting from the expansion of the liquid, when reading at a high temperature, it is necessary either to make up the solutions at the temperature at which they are to be read or to make correction by

[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 81, p. 175.

[b] Principles and Practice of Agricultural Analysis, *3:* 267.

means of a factor. In the present work an empirical factor, established for solutions of pure sucrose, was employed.

The specific rotation of levulose varies both according to temperature and according to concentration, which is expressed best by the general formula of Jungfleisch and Grimbert:

$$[\alpha]_D t = -[101.38 - 0.56t + 0.108(c - 10)]$$

For a 1 per cent solution of levulose the variations on the Ventzke scale (200-mm tube) for 1° C would be 0.0323. The method of calculation would be as follows:

$$\text{Per cent of levulose} = \frac{100\ (P' - dP)}{.0323(t' - t)\ W}$$

W = weight of substance in 100 cc solution
P′ = polarization at high temperature (t')
P = polarization at low temperature (t)
d = factor for expansion or $1 - 0.000523\ (t' - t)$.

In the analysis of molasses and low-grade sirups, 10 grams were weighed and made up to 100 cc. For the better grade of sirups and raw sugars 25 grams were weighed and made up to 100 cc. For juices 100 grams were weighed and after clarification made up to 110 cc; correction was made for the dilution in the latter case by increasing the readings by one-tenth. Clarification was effected in every instance by using a minimum quantity of lead subacetate.

Combination method.—For the estimation of levulose and dextrose in the presence of sucrose the following formulæ have been proposed, polarization being made up at 20° C:[a]

$$L = \frac{a\,R + S - P}{a + b}$$
$$D = R - L$$

In these formulæ the terms of the equations have the following significance:

L = Per cent of levulose
D = Per cent of dextrose
P = Polarization
S = Per cent of sucrose
$a = \dfrac{\text{Specific rotation of dextrose}}{\text{Specific rotation of sucrose}} = +0.797$
$b = \dfrac{\text{Specific rotation of levulose}}{\text{Specific rotation of sucrose}} = -1.354$
R = Per cent reducing sugars.

There are two sources of error in the above method of calculation: (1) The slight reducing influence of sucrose upon the Fehling solution is not taken into account. (2) The difference in reducing power of dextrose and levulose is not considered. The above formulæ have, therefore, been slightly modified, in order to correct for these disturbing influences.

The reducing action of sucrose upon Fehling solution is a variable quantity, but is dependent largely upon the degree of concentration. This is shown in the following table. The determinations of dextrose were made by Allihn's method.

[a] Remy, Bul. de l'association des chemistes, 1903–4, p. 1002; Buisson, loc. cit., p. 499.

TABLE I.—*The influences of sucrose upon Fehling solution in the determination of dextrose (25 cc of solution used).*

Sucrose.	A. Dextrose taken.	B. Dextrose found.	Difference (B−A).	Calculated correction (sucrose divided by 100).
Gram.	*Gram.*	*Gram.*	*Gram.*	*Gram.*
None.	0.1878	0.1877	.....	.....
0.22	.1397	.1417	.0020	.0022
.41	.0985	.1038	.0053	.0041
.65	.0418	.0491	.0073	.0065
1.03	.1593	.1727	.0134	.0103

A subtraction of one one-hundredth of the weight of sucrose in the 25 cc of solution from the weight of dextrose found will give approximately the true weight of dextrose. Such a correction, it is felt, is more or less of an arbitrary character, yet the results obtained, in our limited experience with the method, seem to justify its use. A concentration of 1 gram of sucrose to 25 cc of solution was the maximum employed; for amounts exceeding this concentration a different correction would no doubt be required. To correct for the difference in reducing power of dextrose and levulose, use was made of the results of Hönig and Jesser, who have found that the reducing power of levulose, following absolutely the method of Allihn, for all concentrations, bears a constant relation to that of dextrose. For the same weight of reduced copper 1 part of levulose corresponds to 0.916 part of dextrose. Using this factor the method of calculation is as follows (see previous formulæ):

(1) $D+0.916\ L=R$ (reducing sugars as dextrose by Allihn's method after correcting for sucrose).

(2) $aD-bL=P-S$.

$$L=\frac{aR+S-P}{0.916a+b}=\frac{0.797\ R+S-P}{0.73+b}.$$

$$D=R-0.916\ L.$$

The value b (specific rotation of levulose, divided by the specific rotation of sucrose) is dependent largely upon the temperature of the solution during polarization; also, but to a much less degree, upon the concentration. The ratio as calculated from the formula of Jungfleisch and Grimbert for different temperatures and concentrations is given herewith, and in the above formula is to be taken as a positive quantity.

TABLE II.—*Ratio of specific rotation of levulose to that of sucrose.*

Temperature.	Concentration of solution.				
	1 per cent.	2 per cent.	3 per cent.	4 per cent.	5 per cent.
° C.					
15	1.3835	1.3851	1.3868	1.3885	1.3901
20	1.3414	1.3431	1.3447	1.3463	1.3480
25	1.2994	1.3010	1.3026	1.3043	1.3059
30	1.2573	1.2589	1.2605	1.2621	1.2638

The application of the above methods to the analysis of solutions containing known percentages of levulose, dextrose, and sucrose is given in the following table:

TABLE III.—*Analysis of solutions containing known percentages of levulose, dextrose, and sucrose.*

No.	Levulose.			Dextrose.		Sucrose.	
	Amount taken.	Optical method.	Combination method.	Amount taken.	Combination method.	Amount taken.	Clerget method.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1...	0.87	0.92	0.77	0.88	1.00	26.81	26.87
2...	1.87	1.72	1.80	1.89	2.09	14.94	15.03
3...	3.30	3.26	3.37	3.35	3.44	41.34	41.44
4...	4.10	4.11	4.13	4.14	4.22	32.59	33.77
5...	4.60	4.80	4.75	4.65	4.81	4.71	4.89
6...	7.25	7.40	7.29	7.35	7.30	21.76	21.96
7...	8.16	7.90	8.38	8.25	8.27	25.08	25.35

The results show that both methods for the determination of levulose give results which agree very closely with the actual amounts taken, the error in no instance exceeding 0.26 per cent.

The analysis of a number of cane juices, at the various stages of growth of the cane, is shown in Table IV.

TABLE IV.—*Analysis of sugar-cane juices.*

Date.	Polarization.	Sucrose, Clerget method.	Levulose.		Dextrose, combination method.
			Optical method.	Combination method.	
	°V.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
July 15	− 0.10	0.76	1.66	1.78	1.89
August 15	+ 3.30	4.12	1.65	1.91	2.11
September 9	+ 5.60	5.97	1.76	1.57	1.83
September 23	+ 6.80	7.32	1.57	1.59	2.03
October 1	+ 8.70	8.93	1.32	1.28	1.80
October 12	+11.25	11.60	1.22	.97	1.18
November 4	+13.20	13.60	.77	.53	.41
November 18	+15.80	15.86	.50	.21	.29
November 28	+18.40	18.29	.25	.02	.18

The results for the levulose determinations by the two methods show a fair degree of uniformity, the greatest difference in any case being 0.29 per cent. The results by the optical method seem to run a little high, especially in the juice from mature canes, the percentage of levulose in some cases exceeding the total reducing sugars.

In Table V the application of the methods to the analysis of a number of sirups, molasses, and raw sugars is shown.

TABLE V.—*Analyses of various sugar products by different methods.*

Product.	Polarization.	Sucrose, Clerget method.	Levulose.		Dextrose, combination method.
			Optical method.	Combination method.	
	°V.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Cane sirup	59.9	62.33	3.31	3.32	2.22
Open kettle molasses	51.0	50.33	5.52	5.03	7.93
Diffusion process molasses	25.2	34.83	11.90	13.71	9.43
Commercial centrifugal molasses (1)	22.2	31.25	15.14	14.96	12.18
Commercial centrifugal molasses (2)	23.9	28.08	16.05	14.71	17.98
Commercial centrifugal molasses (3)	16.0	26.89	15.76	15.55	12.22
Raw sugar (1)	72.65	76.28	5.97	6.44	5.20
Raw sugar (2)	79.45	81.62	2.37	2.80	1.45
Raw sugar (3)	79.05	82.38	4.08	4.25	2.40
Raw sugar (4)	80.50	83.56	3.91	3.80	2.11
Raw sugar (5)	81.60	83.66	4.98	2.90	1.92
Raw sugar (6)	86.30	87.74	1.21	1.10	.....

The above results for levulose by the two methods are fairly concordant, with one or two exceptions. Several samples of the molasses were hard to clarify and the difficulty in making the readings may explain a few of the discrepancies; the presence of other carbohydrate bodies in small amounts, such as caramel, may also have exerted a disturbing influence. The methods are unquestionably more applicable to the analysis of juices, sirups, and molasses than to sugars. A large excess of sucrose in the presence of small amounts of reducing sugars necessarily affects the accuracy of the determination. In sugar No. 6, for example, the percentage of levulose exceeded slightly the total percentage of reducing sugars.

To summarize, it may be said that while neither the optical nor the combination method for the determination of levulose, as they stand at present, is as exact as the polariscopic determination of sucrose, yet they do give a fairly close approximation. It is therefore recommended that the succeeding referee take up work along this line, as the perfection of a method for the determination of levulose and dextrose in the presence of sucrose would be valuable.

II. The Nature of Various Gums Found in Sugar-Cane Products.

But very little work has been done by the association toward formulating methods for the identification and analysis of that large class of vegetable compounds which have been loosely classified under the name of gums. The time is fast approaching, however, when more attention must be paid by our chemists to this important group of substances. The various bodies known as gums may be divided into three classes: (1) The hemicellulose gums, of which wood-gum is the best-known type. This class of gums plays an important part among the nutritive elements of our feeding materials; (2) the exudation gums, such as gum arabic, gum tragacanth, etc. These gums enter into the manufacture of many commercial products, and satisfactory methods of analysis for their valuation have long been needed; (3) the fermentation gums, such as dextran and levulan. A knowledge of the constitution of these gums is frequently of great importance to the mycologist and bacteriologist.

A study of the numerous gums occurring in the various products of the sugar cane has been lately undertaken at the Louisiana sugar experiment station by the associate referee on special methods of sugar analysis. These gums may be divided into two classes; the first class consists of those gummy products derived naturally from the hemicelluloses of the cane fiber, comprising xylan, araban, and traces of galactan.

The amount of these gums which passes into the juice, sirup, and molasses will vary according to the pressure of the rollers and the degree of maceration which the cane receives during the process of milling. The quantity of gums thus expressed also varies with the variety of cane. The second class of gums found in sugar-cane products do not occur naturally in the cane, but are the result of fermentation processes which set in either before or after the expression of the juice. Dextran, cellulan, mannan, levulan, and levan are examples of such fermentation gums. The above gums of both classes are all precipitated from solution by means of alcohol and in this way are separated from the sugars. The alcoholic precipitate frequently contains a considerable quantity of mineral matter, organic acids, and albuminoids, but by dissolving in hot water and precipitating with alcohol, acidified with hydrochloric acid, a considerable quantity of these impurities are removed and the gums are obtained in a much purer condition. The gums being colloidal carbohydrates are easily resolved by hydrolysis with acids into sugars and the identification of the sugars thus formed constitutes one of the principal means for determining the nature of the gums. The properties of a few of the gums obtained from sugar-cane products are given below:

Xylan $(C_5H_8O_4)_n$.—This gum has been found in small amounts with traces of araban and galactan in all juices, sirups, and molasses obtained from sugar cane. Xylan, as prepared from sugar cane by the method of Salkowski, possesses a specific rotation of −88.8. On hydrolysis with hydrochloric acid, by the process of Councler, xylose is formed almost quantitatively. If present in large amounts the xylose may be separated in crystalline form and polarized ($[\alpha]_D = +18.4$). If present in only small amounts the solution to be tested is evaporated to a sirup and oxidized with a few drops of bromin in the presence of cadmium carbonate. After standing for several hours the solution is warmed, filtered, and evaporated If xylose is present characteristic crystals of the double bromid and xylonate of cadmium ($Cd\ Br\ C_5H_9O_6H_2O$) are obtained (Bertrand's reaction).

Araban $(C_5H_8O_4)_n$.—This gum occurs associated with xylan among the hemicelluloses components of the cane. On hydrolyzing by Councler's process arabinose is produced almost quantitatively. In case xylose or other sugars are present, the arabinose is precipitated from the solution as an insoluble hydrazone by means of benzylphenylhydrazin or diphenylhydrazin. From the weight of hydrazone thus obtained the amount of arabinose or araban can be calculated. By decomposing the hydrazone with formaldehyde or benzaldehyde the arabinose may be isolated in crystalline form ($[\alpha]_D = +104.1$). To determine the relative amounts of xylan and araban in mixtures, the total amount of both pentosans is estimated as xylan by Krober's table. Having determined the araban by the hydrazone method, the per cent of xylan equals the per cent of total pentosans minus 0.83, multiplied by the per cent of araban.

Galactan $(C_6H_{10}O_5)_n$.—This gum is found in the products from Louisiana cane only in traces. Prinsen-Geerligs, however, has found it in the products from Java canes in determinable amounts. It is determined, according to the official method, by oxidation with nitric acid and weighing the mucic acid formed.

Dextran $(C_6H_{10}O_5)_n$.—This belongs to the fermentation gums and does not occur in normal cane products. The writer has found dextran to exist under three different modifications—an exceedingly soluble, a gelatinous, and an insoluble form. The insoluble and gelatinous varieties of dextran are easily brought into solution by means of a little caustic alkali. The specific rotation of several samples of this gum, isolated from various cane products, was found to be +200, which is about three times that of sucrose. The presence of dextran may, therefore, and frequently does, introduce a considerable error into the work of analysis. Juices and sirups of an apparent purity of over 200 have been found; its presence in molasses and sirups may also lead one to suspect erroneously an adulteration of the sample with com-

mercial glucose. On hydrolysis with acids dextran is converted into dextrose. Mannite is frequently found associated with dextran as a fermentation product.

Cellulan $(C_6H_{10}O_5)_n$.—This gum was found occurring in a sample of sirup left over in the tanks of a sugarhouse. It consisted of large gelatinous lumps, resembling somewhat the insoluble modifications of dextran; it differs from the latter, however, in being insoluble in alkali. On boiling with dilute alkali the gum contracts in volume, yielding a dense white mass which gives all the reactions characteristic of cellulose (coloration with chlorid of zinc and iodin, and solubility in cuprammonium).

Mannan $(C_6H_{10}O_5)_n$.—In cane juices, sirups, and molasses, which have undergone fermentation with yeast and other organisms, mannan may often be detected in the deposits of cellular matter. Mannan is best recognized and determined by hydrolyzing the gum with acid and precipitating the mannose from solution in the cold with phenylhydrazin. The insoluble mannose hydrazone settles out in a few hours, after which it is filtered off and weighed.

Levulan $(C_6H_{10}O_5)_n$.—This gum may also be found in the cellular deposits resulting from certain fermentations. It has a specific rotatory power of −221. The gum has been found in beet molasses as large gelatinous masses resembling dextran, but this modification has not been reported thus far in any cane products. On hydrolysis with acid, levulan is converted into levulose.

Levan $(C_6H_{10}O_5)_n$.—This gum was found occurring in raw sugars by Smith and Steel in Australia. It yields levulose on hydrolysis the same as levulan, but differs from the latter gum in having a specific rotation of only −41. Levan has not been discovered thus far in any Louisiana products.

Other gums of an unknown character have been separated from cane molasses, the identification of which is at present under way. The above investigations, however, have thus far been necessarily limited to the products affecting the cane-sugar industry. It is highly desirable that this work be extended by the association to include other classes of gums, in order that satisfactory methods may be devised for the analysis of this important class of vegetable substances.

REPORT ON METHODS FOR THE ANALYSIS OF MOLASSES.

By H. E. Sawyer, *Associate Referee on Sugar.*

The problem which has received most of my attention during the year is that referred to in my paper on Methods of Molasses Analysis, read at the twentieth convention of the Association of Official Agricultural Chemists, and published on page 175 of Bulletin No. 81 of the Bureau of Chemistry. I have sought to ascertain the means by which very dark molasses may be analyzed expeditiously and most accurately, giving special attention to the feasibility of making the polarizations, both invert and direct, in a solution of only one-fifth the usual concentration. This question, apparently simple, has called for a minute investigation of the sources of all the errors which may affect the final result of a sucrose determination by the method of double polarization, and the final answer has not yet been obtained. It has been necessary to study the following points.

(1) Variations in the standards of quartz-wedge saccharimeters.

(2) Irregularities of graduation throughout the scales of such saccharimeters.

(3) Precision attainable in observations with such saccharimeters under varying conditions as to intensity of illumination and color of solution.

(4) Practical effect upon polarization, through change of specific rotary power, of employing a solution of one-fifth the usual strength.

(5) Necessity for having, for use with this dilute solution, another constant or factor for the denominator of the Clerget equation than that employed with the solution of usual concentration.

(6) Action on the sugars of molasses, in solutions of varying concentration, of different preparations of lead acetate, varying in basicity and added in varying amounts.

A paper has already been published on the first of the preceding subjects and an extension of the investigation, together with a study of the second subject, has been carried on during the summer. Publication will, however, be withheld until the facilities of the Bureau of Standards permit the accurate standardization of the quartz plates which have been employed. This probably will be within two or three months.

A study of subject No. 3 is now being made, and No. 4 is shortly to be taken up. No. 5 will not be taken up until cold weather. Subject No. 6 is more important than any of the others, if, as Pellet has claimed, the levulose of cane molasses is precipitated by basic acetate of lead. A very careful study of this question is now being made. The discussion of the subject will be given in two papers, the first of which, Basic Lead Acetate Solutions: Their Preparation, Analysis, and Composition, is practically ready for publication. The second paper, on The Action of Lead Acetates on the Sugars of Cane Molasses, will follow shortly.

In addition to the subjects enumerated above, the associate referee has studied comparatively the various precipitants which may be employed for removing the excess of lead from a clarified solution previous to its examination for reducing sugars. It was found that the neutral oxalate of potassium gives much better results than the carbonate and sulphate of sodium, which now are used, and the substitution of the oxalate for the carbonate and sulphate in the methods of the association is recommended.

Recommendations.

In addition to the recommendation just made, it is suggested that the sugar referee or one of his associates for the coming year be requested to submit the analytical method which has been outlined, and which will be published in detail during the winter, to a collaborative test in comparison with the usual method of molasses analysis.

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The following paper was submitted by Mr. Sawyer for publication in connection with his report:

ANALYSES OF MOLASSES PRODUCED BY DIFFERENT METHODS OF MANUFACTURE, AND COMPARISON OF METHODS FOR DETERMINING TOTAL SOLIDS.

By J. E. Halligan, *Audubon Park, New Orleans, La.*

In Table I are found analyses of seven Louisiana molasses from different sections of the State and resulting from different methods of manufacture.

Table I.—*Analyses of molasses obtained by different methods of manufacture.*

Determinations.	1 Common centrifugal.	2 Common centrifugal (diffusion).	3 Common centrifugal.	4 Common centrifugal.	5 Common centrifugal.	6 Open-kettle centrifugal.	7 Open-kettle centrifugal.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Sucrose	26.89	34.83	31.25	28.08	30.73	48.11	50.83
Levulose	15.58	13.68	15.00	14.60	17.19	8.84	5.08
Dextrose	14.27	9.72	12.53	18.01	13.92	8.68	8.30
Gums	3.16	2.47	2.41	2.02	2.56	1.00	.57
Free acid	1.74	2.35	2.01	1.07	1.27	.77	.73
Combined acid	4.76	2.14	3.16	1.89	2.30	1.74	2.17
Amids	2.49	2.50	1.38	1.31	2.25	1.15	.58
Albuminoids	.39	.50	.31	.25	.38	.04	.11
Lime (CaO)	1.43	.73	.74	.99	.99	.27	.19
Phosphoric acid (P_2O_5)	.19	.84	.84	.11	.14	.14	.33
Sulphuric acid (SO_3)	1.55	1.00	1.27	1.25	1.60	.48	.19
Other ash constituents	5.96	8.81	7.70	4.14	6.12	2.93	2.82
Total	78.41	79.57	78.60	73.72	79.45	74.15	71.90
Total solids	76.94	78.57	79.98	73.54	79.07	72.65	72.14
Brix	85.23	87.84	88.16	79.64	88.32	a71.63	72.60
Total reducing sugar as dextrose (Allihn)	27.00	22.25	26.27	31.38	29.67	16.78	12.95

a Low Brix probably due to fermentation.

The methods pursued in making these determinations were as follows:

Sucrose.—Normal weight was made up to 200 cc and double polarized. Readings were made in 200 or 100 cc tubes, according to the clearness of the solution.

Reducing sugar.—Determined by Allihn's method for the determination of dextrose. Calculations were made from Allihn's table for the determination of dextrose.

Levulose and dextrose.—Determined by formula. (See article by the associate referee on special methods.)

Gums.—One gram of molasses was dissolved in 10 cc of hot water. One hundred cc of 95 per cent alcohol was then added and the solution was allowed to stand until the flocculent precipitate had settled. The clear solution was decanted on a gooch and the precipitated gums were washed twice with 95 per cent alcohol and dried to constant weight. The precipitate was then ignited and the gums determined by subtracting the ash and combined acid (determined from the alkalinity of the ash).

The total nitrogen was figured as protein. The albuminoids were determined by Stutzer's method. The difference between the albuminoids and protein is taken as amids.

Sulphuric acid.—Three grams of molasses were dissolved in 25 cc of water. Concentrated permanganate of potash solution was added until the solution assumed a

pink coloration and hydrochloric acid was added until the color was destroyed. The solution was then filtered to get rid of impurities and precipitated with barium chlorid. The permanganate of potash converts any sulphites that may be present to sulphates. All the samples were examined for sulphites and none was found.

Total solids.—Two grams of molasses were dried in a water oven at 98° C for 10 hours.

Brix.—An equal weight of water and molasses was taken and the result multiplied by two. The total solids by Brix is not applicable to the analysis of molasses. This has been effectually demonstrated by the work of Geerligs of Java.

A comparison of methods on the determination of total solids in molasses was also made. Direct drying for 10 hours is used at this station, for it conforms more nearly to the vacuum method. In all determinations 2 grams of molasses were taken.

TABLE II.—*Comparison of methods for determining total solids in molasses.*

Method.	Constant weight.	2 hours.	4 hours in air bath at 105° C.	10 hours.	20 hours.	30 hours.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
In vacuo	76.44	.....	.....	.....	.....	.....
Paper coil method	.....	.....	73.18	.....	.....	.....
Direct drying	.....	.....	.....	76.94	74.14	73.31
Pumice and 1 volume of alcohol	.....	77.39	.....	75.10	73.74	73.19
Pumice and 2 volumes of alcohol	.....	78.01	.....	75.46	73.89	72.68
Official method	.....	78.05	.....	75.85	74.19	73.23
Direct, with 10 cc of alcohol	.....	82.81	.....	78.67	75.15	73.63

The following paper on the analysis of sugar beets, coming properly under the head of chemical methods, was submitted to the referee on sugar by Mr. Davoll, formerly associate referee on this subject, for publication, and approved by him:

A RAPID METHOD FOR BEET ANALYSIS.

By DAVID L. DAVOLL, Jr., *Caro, Mich.*

In the chemical control of the various stages of a manufacturing operation, as in iron and steel work, sugar making, etc., or the assay of the finished product for the purpose of accurate standardization, as in pharmaceutical preparations and similar products, or in determining the purchasing price of raw material when rated according to the percentage of some valuable constituent, all efforts are bent to securing results quickly. Reasonable accuracy is, of course, always demanded, and scientific precision continues to be the subject of earnest endeavor. It is gratifying to note that scientific exactness is attained together with the requisite speed in many commercial analytical methods.

While the determination of the percentage of sucrose in a sample of sugar beets requires in itself something like 1 to 1½ hours, it is quite necessary that a "house" cutting 1,000 to 1,200 tons of beets per day of 24 hours should be in a position to make in its receiving laboratory from four to five hundred analyses per day of 10 working hours and with very small working force. In pleasant weather 500-ton houses must handle this number.

Efforts to introduce the method known as that of hot-water digestion have failed, because a chemist with one assistant can only hope to dispose of about 100 samples a day with any degree of accuracy. There is also a hesitancy about adopting any of the instantaneous methods for well-known reasons. The alcoholic methods

are, of course, out of the question, excepting as an occasional check upon the water methods. The high price of alcohol, its mobility and volatility, together with the demand for too close adherence to niceties in manipulation, exclude its use. There is also danger of precipitating lead saccharate in alcoholic media.[a]

The frozen condition of the beets offers serious obstacles to the indirect analysis by the juice method and the use of a transposing factor. The freezing of the beets is apt to occur in our most northern States any time after November 1, but it is sometimes delayed in an especially open and mild season until December 1, as was the case in 1899 and again in 1904 in Michigan. One would also hesitate to analyze frozen beets by any of the methods of instantaneous cold-water digestion since any efficient thawing of the beets previous to weighing out the normal or any multiple of it would almost certainly result in financial loss to the purchaser. Of course, an attempt to warm the mass after weighing would be quite as circumstantial and time-consuming in operation as hot digestion itself.

In detail, the method of hot-water digestion is as follows:

Ten cc to 16 cc of solution of lead subacetate of 54.3° Brix are placed in a 201.2 cc sugar flask and 52.096 grams of shredded beet are introduced by means of a glass rod assisted with a spray of water, the volume being finally completed to about 190 cc. A little ether is added to beat down the foam and the whole is heated in a water bath at 80° C for 30 minutes, rotating the flask from time to time to promote extraction and facilitate the escape of air bubbles. Water is added from time to time so that the volume is completed to the mark at the end of 30 minutes. Cool to the room temperature, add more ether to dissipate any remaining foam, dilute with water to the mark, mix thoroughly, and filter.

Beet pulp of varying degrees of coarseness may be used with success in this method, although the time of digestion should be extended in proportion to the coarseness. The introduction of the pulp into the flask is painstaking and time-consuming to a degree dependent upon the fineness of the pulp, the diameter of the neck of the flask remaining constant. A medium fineness and shredded pulp give the most trouble. The rotation necessary to secure proper extraction and eliminate occluded air requires considerable attention and the repeated addition of ether, and even then good results are not always obtained. Many careless operators neglect the rotation during heating entirely, and this is most apt to happen when many samples are to be analyzed. Where 26.048 grams are used in 200.6 cc dilution the manipulation is more satisfactory, but the use of a 200 mm tube doubles any error in reading. A double normal should always be taken in commercial work, as it is more representative of the original sample, since perfectly intimate mixing can not always be counted upon where the chemist is dependent upon the unscientific helper to prepare the sample. Rapid and at the same time uniform cooling can not be obtained without stirring the flask contents, which is very difficult. After adding the final quantity of water, the intimate mixing of the contents, which is absolutely essential, is rendered difficult by the presence of the pulp, which plugs up the constricted portion of the neck.

The author has sought to overcome the objections to the method of hot-water digestion mentioned above by substituting a beaker for the flask and finally completing the mass to a certain weight, i. e., 209.2 grams, instead of volume. A definite weight of water, and therefore a fixed volume also, can not be added to a normal or multiple thereof of shredded beet unless it be first ascertained that the diminishing volume of the definite weight of beet, due to increased specific gravity of the constituent juice with rise of sugar percentage, is without influence upon the polarization within the limits of accuracy of the saccharimeter. The Kaiser-Sachs modification of Pellet's instantaneous diffusion directs the weighing of the quantity of water, i. e., 172 grams, where a normal of pulp is used, into the counterpoised flask containing the lead solution. In the modification to this same instantaneous method by cold

[a] J. Weisberg, Stammer's Jahresbericht, 1887, 27: 159. Sucrerie belgae, 1887.

digestion, Fr. Sachs and A. Le Docte, while measuring a 5 cc solution of lead subacetate and 177 cc water upon 26.048 grams of shredded beet contained in a copper capsule, in effect use the principle of weighing. Both of these methods are briefly outlined in Spencer's Handbook for Beet Sugar Chemists, but the original publications are inaccessible to the writer.

If a strictly representative juice could be expressed from the beet it would be possible to ascertain its specific gravity and thus calculate the gross weight of beet pulp, lead subacetate solution, and water necessary to complete the volume to 201.2 cc for beets of different sugar percentages. Obtaining the total solids in the beet and from this subtracting the marc, while giving the real Brix or total solids in the juice, would not give the Brix by "spindling," having its equivalent in specific gravity, for well-known reasons. We have abundant reason to believe that beets showing the same percentage of sugar contain juices of different specific gravities. This is shown by the variation in the gross weights of flask contents, corrected, in the accompanying table. The use of 14 cc of lead subacetate solution of 54.3° Brix where a double normal of pulp is used in 200 cc dilution has been adopted. This is on account of the frequent hardness of water in general use, which impoverishes the lead solution by reason of sulphate and acid carbonate present. Ordinarily the quantity of lead subacetate solution to be used may vary according to the condition of the beet, whether it be fresh and normal, or unripe, spoiled, frozen, or has been preserved in silos. At the moment of adding the basic lead acetate the chemist can scarcely be expected to detect any of these conditions and will be guided considerably by the season, by experimentation with various quantities, and by noting the effect of lead solution upon the clear filtrate, always being generous rather than sparing of the quantity of lead. Should less lead solution be indicated and fewer cubic centimeters be taken, by simple calculation the gross weight of flask contents may be made up to smaller mass in allowance for this.

To ascertain the correct weight to which beet pulp, lead subacetate solution, and water should be adjusted when mixed, digested, cooled to 20° C, and diluted to exactly 201.2 cc, appended analyses were made in the following manner:

The beets were purposely selected so as to get as many types as possible as regards shape, size, degree of ripeness, sugar content, and effect of freezing. In the case of large, woody, or, on the other hand, of typical, wedge-shaped, thoroughbred beets, the selection represents the pick of five hundred to six hundred tons passing along the conveyor to the automatic scale. The machines for reducing the beet to a pulp need not be considered. The weight of the clean dry flask was carefully ascertained and its capacity in Mohr cubic centimeters determined. The latter was found to vary between 200.76 cc and 201.2 cc, which, while it influences the weight of the contents and is of importance in this experiment, does not affect the polarization. Fourteen cubic centimeters of lead subacetate were run into the flask and a double normal (52.096 grams) of shredded beet introduced with enough water to give a volume of 180 to 190 cc. Flask and contents were then placed in a water bath previously heated to 80° C and maintained at this temperature throughout the digestion, which lasted 30 minutes.

During the digestion the flask was frequently rotated and water added from time to time so that at the completion of the operation the volume was about 201.2 cc. Flask and contents were then cooled to the room temperature by immersing in cold water. By means of a rubber tipped glass rod and a fine spray of water the lead solution, lead precipitate, or fine beet pulp was rinsed down to below the graduation and the volume finally adjusted. The externally clean and dried flask and contents were then weighed, 10 milligrams being the smallest weight employed. The contents were next intimately mixed, filtered, and polarized in the usual manner. The temperature of the solution was also noted. The average weight of the flask contents after digestion, fully corrected for volume and temperature to bring them up to a standard of 201.2 cc and 20° C, shows an average, in round numbers, of 209.2 grams. This may be taken, therefore, as the correct weight to which the mass must be adjusted in water digestion for beets in the receiving laboratory or for cossettes at the diffusion battery.

In the column marked I, in the accompanying table, the polarization has been corrected to conform to the prescribed volume of 201.2 cc and in no case does the correction exceed 0.036 per cent plus or minus, which is well within the limits of accuracy of the instrument. Upon the basis of these corrected readings is calculated the percentage of sugar in the solution that would result had the weight been purposely changed at the end of the analysis to a uniform mass of 209.2 grams, which is shown in the thirteenth column, marked II. The difference in the sugar content caused by this change of weight to a constant quantity is shown in the fourteenth column. In some instances there is no variation at all, in others it is inappreciable, and in all cases, with beets containing less than 17 per cent of sugar, it is well within the limits of accuracy of the polariscope. For beets containing over 17 per cent of sugar it may be found necessary, after collecting further corroborative data, to subtract 0.10 per cent from the polariscopic reading for a weight of 209.2 grams. In one instance the calculated variation is seen to be 0.09 per cent, which can scarcely be accounted for and which will be taken up in further investigations.

In this table there is also shown the constant increase in weight with increase in sugar content. Though this relation is somewhat irregular the extremes are certainly well within limits demanded even in a scientific analysis. It should be noted that these analyses were made upon individual beets in the majority of cases. This was for the purpose of detecting any great irregularities due to individuals. But in a receiving laboratory, where from ten to one hundred beets are united for one test, any peculiarities would sink into insignificance and exert no influence other than that dependent upon the density of the juice and therefore upon the sugar content.

The author proposes to dispense with the use of a flask altogether in the analysis of beets by the method of hot-water digestion, substituting therefor a glass beaker, which is superior to a container of any other material because its weight can be kept constant. Since beakers can now be had of considerable thickness and are long-lived when subjected to sudden changes of temperature often repeated, the danger from breakage is slight, especially in a properly constructed bath accommodating twenty-five to fifty samples. Experiments along this line will be repeated on the next crop.

TABLE 1.—*Comparison of the weighing and volumetric methods in the analysis of sugar beets.*

Weight of flasks.	True capacity of flasks.	Weight of flask and contents.	Net flask contents.	Temperature.	Flask contents corrected to 20° C and 201.2 cc.	Polarization.	Polarization corrected to 209.2 grams in 201.2 cc at 20° C.	Number of beets.	Weight of each beet.	Physical characteristics.	I.—Polarization corrected to 201.2 cc.	II.—Polarization corrected to 209.2 grams.	Difference between I and II.	Date.
Grams.	*Cc.*	*Grams.*	*Grams.*	*° C.*	*Grams.*				*Grams.*					
64.120	201.20	272.60	208.48	21	208.52	8.8	8.770	1	2,370	Woody, broad	8.800	8.770	−0.030	Dec. 7
58.400	200.91	266.17	208.06	24	208.24	10.1	10.052	1	.....	Woody, underripe	10.085	10.037	−0.048	Nov. 14
64.120	201.20	272.50	208.38	23	208.51	10.3	10.265	1	.....	Very large and woody	10.300	10.265	−0.035	Nov. 11
58.400	200.91	267.38	209.27	18	209.19	11.0	11.000	1	1,430	Woody, typical	10.984	10.984	0.000	Dec. 6
55.800	200.76	264.20	208.84	18	208.76	11.5	11.475	1	2,165	Woody, broad	11.475	11.450	−0.025	Dec. 6
53.520	201.13	261.95	208.50	24	208.68	11.8	11.769	1	.....	Woody, underripe	11.800	11.769	−0.031	Nov. 14
64.120	201.20	272.80	208.68	18	208.60	.....	11.864	1	1,670	Woody, broad	11.900	11.864	−0.036	Dec. 6
53.520	201.13	261.20	207.75	18	207.67	11.9	11.810	1	2,020	Woody, juicy, typical	11.900	11.810	−0.090	Dec. 6
55.800	200.76	263.75	208.39	25	208.62	.....	11.866	1	.....	Woody, underripe	11.874	11.840	−0.034	Nov. 14
64.120	201.20	272.45	208.33	25	208.56	12.0	11.962	1	.....	.....do	12.000	11.962	−0.038	Nov. 14
68.920	201.06	277.60	208.82	23	208.95	12.0	11.985	1	.....	.....do	11.992	11.977	−0.015	Nov. 14
68.920	201.06	277.50	208.72	25	208.95	12.6	12.593	1	.....	.....do	12.591	12.584	−0.007	Nov. 14
64.120	201.20	272.82	208.70	23	208.83	12.6	12.577	1	.....	.....do	12.600	12.577	−0.023	Nov. 13
65.080	200.88	273.68	208.92	18	208.84	12.8	12.777	1	.....	Woody, broad	12.780	12.757	−0.023	Dec. 6
58.400	200.91	267.10	208.75	23	208.88	12.8	12.779	1	Small.	Typical	12.781	12.760	−0.021	Nov. 11
68.920	201.06	277.12	208.34	23	208.47	12.9	12.853	1	Large.	Very juicy	12.891	12.844	−0.047	Nov. 11
68.920	201.06	277.82	209.04	21	209.08	13.1	13.092	1	620	Typical	13.091	13.083	−0.008	Dec. 7
55.800	200.76	264.19	208.83	23	208.96	13.3	13.284	.....	.....	25-pound field sample	13.270	13.254	−0.016	Nov. 9
64.120	201.20	272.85	208.73	25	208.96	13.6	13.583	1	1,390	Fibrous	13.600	13.583	−0.017	Nov. 23
53.520	201.13	262.52	209.07	15	208.89	13.7	13.679	1	475	Typical; frozen hard	13.695	13.674	−0.021	Dec. 17
55.800	200.76	264.32	208.96	21	209.00	13.7	13.686	1	320	.....do	13.670	13.656	−0.014	Dec. 7
65.080	200.88	274.12	209.36	25	209.59	13.9	13.927	1	574	25-pound field sample	13.877	13.904	+0.027	Nov. 24
68.920	201.06	278.04	209.26	23	209.39	13.9	13.913	.....	.....	Typical	13.890	13.903	+0.013	Nov. 9
53.520	201.13	262.71	209.26	21	209.30	14.0	14.000	1	420	.....do	13.894	13.901	+0.007	Dec. 7
55.800	200.76	264.10	208.74	23	208.87	14.0	13.977	1	Large.	Woody, underripe	13.969	13.946	−0.023	Nov. 13
55.800	200.76	264.72	209.36	15	209.18	14.0	14.000	1	350	Typical; frozen hard	13.969	13.969	0.000	Dec. 17
68.920	201.06	278.15	209.37	18	209.29	14.1	14.094	1	1,620	Woody, broad	14.090	14.084	−0.006	Dec. 6
55.800	200.76	264.42	209.06	23	209.19	14.2	14.200	1	415	.....	14.169	14.169	0.000	Nov. 11
55.800	200.76	264.60	209.24	22	209.33	14.4	14.409	1	Small.	Typical	14.368	14.377	+0.009	Nov. 26
64.120	201.20	273.53	209.41	25	209.64	14.6	14.632	1	370	.....do	14.600	14.632	+0.032	Nov. 24
58.400	200.91	266.80	208.69	23	208.82	14.6	14.572	1	Large.	Woody, underripe	14.578	14.550	−0.028	Nov. 13
53.520	201.13	262.22	208.77	23	208.90	14.6	14.578	1	Large.	.....do	14.594	14.572	−0.022	Nov. 13
53.520	201.13	262.45	209.00	23	209.13	14.6	14.595	2	405	Typical	14.594	14.589	−0.005	Nov. 20
65.080	200.88	273.97	209.21	15	209.03	14.7	14.687	1	550	Typical; frozen hard	14.676	14.663	−0.013	Dec. 17
58.400	200.91	267.11	209.00	25	209.23	15.2	15.202	2	170	Typical	15.177	15.179	+0.002	Nov. 23
64.120	201.20	273.20	209.08	23	209.21	15.4	15.401	2	785	.....do	15.400	15.401	+0.001	Nov. 20
68.920	201.06	277.94	209.16	23	209.29	15.4	15.407	.....	.....	25-pound sample	15.389	15.396	+0.007	Nov. 10

TABLE I.—*Comparison of the weighing and volumetric methods in the analysis of sugar beets*—Continued.

Weight of flasks.	True capacity of flasks.	Weight of flask and contents.	Net flask contents.	Temperature.	Flask contents corrected to 20° C and 201.2 cc.	Polarization.	Polarization corrected to 209.2 grams in 201.2 cc at 20° C.	Number of beets.	Weight of each beet.	Physical characteristics.	I.—Polarization corrected to 201.2 cc.	II.—Polarization corrected to 209.2 grams.	Difference between I and II.	Date.
Grams.	*Cc.*	*Grams.*	*Grams.*	°*C.*	*Grams.*				*Grams.*					
58.400	200.91	267.75	209.64	21	209.68	15.6	15.637	1	440	Typical	15.576	15.613	+0.037	Dec. 7
65.080	200.88	274.38	209.62	21	209.66	15.7	15.736	1	420	.....do	15.675	15.711	+0.036	Dec. 7
53.520	201.13	262.35	208.90	23	209.03	15.7	15.686	1	Medium.		15.694	15.680	−0.014	Nov. 11
68.920	201.06	277.95	209.17	22	209.26	15.8	15.805	1	660	Typical	15.789	15.794	+0.005	Nov. 26
58.400	200.91	267.40	209.29	25	209.52	15.8	15.825	2	600	.....do	15.777	15.802	+0.025	Nov. 24
55.800	200.76	264.90	209.54	23	209.67	15.8	15.835	1	365	.....do	15.765	15.802	+0.037	Nov. 20
53.520	201.13	262.60	209.15	25	209.38	15.9	15.914	1	435	.....do	15.894	15.908	+0.014	Nov. 24
64.120	201.20	273.69	209.57	23	209.70	15.9	15.940	....	.....	25-pound field sample	15.900	15.940	+0.040	Nov. 9
58.400	200.91	267.82	209.71	15	209.53	16.1	16.127	1	440	Typical; frozen hard	16.077	16.104	+0.027	Dec. 17
64.120	201.20	273.97	209.56	22	209.65	16.1	16.064	1	530	.....do	16.100	16.136	+0.036	Nov. 26
68.920	201.06	271.17	209.39	25	209.62	16.1	16.134	2	225	.....do	16.089	16.123	+0.034	Nov. 23
53.520	201.13	262.82	209.37	23	209.50	16.1	16.124	....	.....	25-pound field sample	16.094	16.118	+0.024	Nov. 10
55.800	200.76	264.72	209.36	25	209.59	16.1	16.131	1	520	Typical	16.065	16.096	+0.031	Nov. 24
55.800	200.76	264.58	209.22	25	209.45	16.3	16.320	2	285	.....do	16.264	16.284	+0.020	Nov. 23
64.120	201.20	273.52	209.40	25	209.63	16.4	16.435	2	370	.....do	16.400	16.435	+0.035	Nov. 23
58.400	200.91	267.55	209.44	23	209.57	16.4	16.430	2	585	.....do	16.374	16.404	+0.030	Nov. 20
53.520	201.13	262.75	209.30	25	209.53	16.5	16.530	1	545	.....do	16.493	16.523	+0.030	Nov. 26
68.920	201.06	278.20	209.42	23	209.55	16.9	16.929	2	450	.....do	16.888	16.917	+0.029	Nov. 20
58.400	200.91	267.92	209.81	22	209.90	17.2	17.260	1	625	.....do	17.174	17.234	+0.060	Nov. 26
53.520	201.13	262.80	209.35	25	209.58	17.3	17.333	2	325	.....do	17.293	17.326	+0.033	Nov. 23
64.120	201.20	274.18	210.06	15	209.88	17.7	17.760	1	470	Typical; frozen hard	17.700	17.760	+0.060	Dec. 17
65.080	200.88	274.75	209.99	22	210.08	17.9	17.979	1	580	Typical	17.871	17.950	+0.079	Nov. 26
68.920	201.06	278.37	209.59	25	209.82	18.0	18.056	1	513	.....do	17.987	18.043	+0.056	Nov. 24
68.920	201.06	278.79	210.01	15	209.83	18.4	18.458	1	530	Typical; frozen hard	18.387	18.445	+0.058	Dec. 17
Average.....			209.11	....	209.20	14.45	.....	....	.....	.....	.....	.....	.....	.....

A brief discussion of the sugar reports followed, Doctor Wiley calling special attention to the importance of the temperature at which polarizations are made, and stating that the international committee recognized that the polarization is seriously influenced by the temperature and scarcely at all by the concentration.

The report of the referee on food adulteration was next received, together with those of the associates on this subject.

REPORT ON FOOD ADULTERATION.

By W. D. Bigelow, *Referee.*

Reports on the following subjects have been made by associate referees not able to be present at this meeting, and I will submit abstracts of them at this time, presenting the papers for publication in full in the proceedings: Colors, distilled liquors, baking powder and baking-powder chemicals, and tea and coffee. Other reports to be made by the associates in person, or by their representatives, are on preservatives, beer, fats and oils, and dairy products. The report on colors, which, as stated in the letter of transmission of the associate, is "voluminous with detailed methods, etc.," is given here only in outline, but will be published in full in circular form for the information of those particularly interested in the subject. This work is in the nature of a compilation, no original researches having as yet been made.

RÉSUMÉ OF REPORT ON COLORS.

By Wilton G. Berry, *Associate Referee.*

General remarks relating to the detection and separation of artificial colors; requirements of the color chemist; purity of dyes; nomenclature of dyes; what constitutes harmful colors; physiological effects; coal-tar color lakes; natural vegetable and animal colors, with botanical and common names; organic lakes; mineral pigments, etc.

I. Wines and alcoholic compounds.
   1. Examination for natural or artificial coloring.
      a. Portes et Ruyssen test.
      b. Paris Municipal Laboratory test.
      c. Dupré test.
   2. Examination for coal-tar colors.
      a. Mansfield test.
      b. Cazeneuve test.
      c. Falières-Ritter test.
   3. Examination for foreign vegetable colors.
      a. Characteristic reactions of tin mordanted fibers dyed with logwood, fustic, quercitron, weld, Persian berries, turmeric, brazilwood, barwood, camwood, orchil and cudbear, cochineal, kermes, lac, etc.
   4. Separation and identification of coal-tar colors.
      a. Sostegni and Carpentieri method.
      b. Arata method.
      c. Wolff-Winterthur method.
      d. Paris Municipal Laboratory method.
      e. Rota's method of identification.
      f. References to various schemes.

I. Wines and alcoholic compounds—Continued.
    5. Special tests for coal-tar colors.
        a. Acid magenta—Girard.
        b. Martius yellow and naphthalen yellow.
        c. Naphthol colors.
        d. Bordeaux red—Casali.
    6. Special tests for vegetable colors.
        a. Caramel—Amthor.
        b. Turmeric.
        c. Cherry juice—Windisch.
        d. Kermes, etc.

II. Brandy, rum, liqueurs, vinegar, etc.
    1. Mansfield method.
    2. Caramel—Crampton and Simons.

III. Fruits, juices, preserves, jam, etc.
    1. Extraction with 80 per cent alcohol.
    2. Characteristic of natural fruits extracted with amyl alcohol and ether.
    3. Detection of cochineal.

IV. Dairy products, fats, oils, etc.
    1. Butter, fats, oils (fresh).
        a. Bujard and Baier test.
        b. Vandriken test.
        c. Leeds method.
        d. Special methods for saffron, tumeric, marigold, annatto (Martin, Moore, Chevallier et Baudrimont), egg yellow (Fendler).
    2. Milk (fresh).
        a. Leach method.
        b. Special test for caramel (Blyth).
    3. Milk (sour).
        a. Blyth method.
        b. Coal-tar color reactions.

V. Nitrogenous substances.
    1. Flesh foods.
        a. Natural colorings.
        b. Abnormal colorings.
        c. Bujard and Baier method.
        d. Klinger and Bujard method.
        e. Spaeth method.
        f. Marpmann method (micros.)
    2. Malt liquors.
        Normal coloring; detection of coal-tar colors; picric acid (Fleck); caramel.
    3. Canned vegetables.
        a. Extraction with alcohol.
        b. Behavior of alcoholic vegetable extracts.

VI. Coffee, tea, spices, etc.
    Coloring matters; facings; azo dyes; indigo; catechu (Hager); Campechy wood (Eder); chicory; sanderswood; turmeric.

VII. Starch preparations.
    1. Coloring matters.
    2. Coal-tar colors, Reichelmann and Lenscher method.
    3. Tropaeolin (Brebeck).

VIII. Confectionery.
    Separation and identification of coloring matters.

REPORT ON DISTILLED LIQUORS.

By C. A. Crampton, *Associate Referee.*

Under date of April 30, 1904, the associate referee sent the following circular letter to all analysts likely to cooperate in the work:

Dear Sir: Your name appears upon a list furnished me by Dr. W. D. Bigelow, as one containing the names of all chemists who had expressed a willingness to collaborate upon the subject of distilled liquors for the Association of Official Agricultural Chemists.

I expect to send out three samples of liquors to each chemist taking part for determination of their character. One sample will be genuine whisky, aged in wood for several years; the second will be factitious spirits obtained from the trade, and the third will be a similar liquor made up in this laboratory. About a pint of each will be furnished, as this will probably be sufficient to determine its character, reliance being placed upon the determination of amount and character of total solids and tests for artificial coloring matter.

In addition to the work on the samples, which will not require much time, I am very desirous of obtaining some comparative data upon the determination of fusel oil by different methods, as this is by far the most troublesome determination pertaining to the analysis of distilled liquors. Any chemist undertaking this will be free to carry it out in his own way, but I should be glad to be informed in advance of the line of experiment he proposes to follow, and will be pleased to render any assistance in my power.

Please inform me at your earliest convenience whether you will take part, and if you desire the samples.

Further instructions will be sent when the samples are forwarded.

Respectfully,

C. A. Crampton,
Associate Referee on Distilled Liquors.

Favorable replies were received from twelve analysts, and a corresponding number of samples was sent out, accompanied by the following letter of instruction:

June 7, 1904.

Dear Sir: I have sent to your address to-day, by express, through the Agricultural Department, a box containing three pint samples of distilled liquors, and a package of fuller's earth. The character of these samples is set forth in my letter dated April 30, and they are sent in accordance with your letter dated ——, expressing your willingness to cooperate.

You will please determine the percentage of alcohol and of total solids in each sample, and make such tests as will enable you to distinguish between the genuine and factitious liquors. The determination of alcohol is not essential, and may be omitted if desired. Inclosed will be found the procedure for detection of foreign color by absorption in fuller's earth, and insolubility in ether, with a reference to the original publications;[a] also the paraldehyde test as modified by Lasché, which we have found very useful. [See page 229.] Any additional tests you have knowledge of can be applied, and should be accompanied by full description in your report.

The copper oxid reducing power of the residue is useful in case sugar has been added as well as caramel coloring.

Your report, with results and suggestions, should be sent in not later than September 16.

As you did not take part in this work last year, I inclose also for your information a carbon copy of the circular letter I sent out June 10, 1903.

Respectfully, yours,

C. A. Crampton,
Associate Referee on Distilled Liquors.

Reports have been received upon five sets of samples, and the results are included in the tabulation which follows.

As indicated in the circular letter quoted above, three samples of spirits were sent to each analyst, simply numbered 1, 2, and 3.

No. 1. Factitious sample made by mixing several trade whiskies.

No. 2. Genuine rye whisky, 5 years old, bottled in bond.

[a] J. Amer. Chem. Soc., 1899, *21:* 355; 1900, *22:* 810.

No. 3. Entirely artificial whisky made up in this laboratory from neutral spirits by addition of caramel and flavoring extracts.

The following table gives the results obtained by different analysts, including also the results of various tests applied to the samples and the conclusions arrived at concerning the character of same:

TABLE I.—*Analytical results obtained by cooperating chemists on the referee's samples of whisky.* (*Results calculated to uniform basis of expression.*)

Determination.	Name of analyst.					
	H. E. Barnard.			Edward Gudeman.		
	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 1.	Sample No. 2.	Sample No. 3.
Specific gravity, at 15½° C.	0.9319	0.9360	0.9320			
Solids (extract):						
Per cent total solids (extract).	.282	.167	.106	0.289	0.164	0.135
Per cent water soluble residue.						
Per cent reducing bodies (dextrose).						
Mineral constituents:						
Per cent ash	.012	.007	.002	.008	.001	Trace.
Alkalinity of ash (cc N/10 per 100 cc).				1.4	.2	
Per cent chlorids				None.	None.	None.
Per cent sulphates				None.	None.	Trace.
Alcohol:						
Per cent alcohol by volume.	51.30	49.32	51.04	52.46	48.98	52.46
Per cent alcohol by weight.	43.69	41.82	43.44	44.80	42.50	44.80
Apparent proof (from gravity).	102.50	98.38	102.40			
Real proof	102.60	98.64	102.80	104.92	97.96	104.92
Acids:						
Free acids (cc N/10 per 100 cc).						
Combined acids (cc N/10 per 100 cc).						
Per cent fusel oil						
Color:						
Degree of color (one-fourth inch cell, brewer's scale).						
Per cent color removed by ether.	8.00	31.0	10.6			
Per cent color removed by fuller's earth.	80.00	66.00	84.00	60.00	30.00	80.00
Qualitative tests, etc.:						
Color				Good.	Good.	Good.
Taste				Fair.	Good.	Poor.
Odor				Fair.	Good.	Medium.
Furfurol reaction (per cent).						
Aldehydes						
Indications of tannins by ferric salts.				Faint.	Strong.	Trace.
Indications of tannins by lead subacetate.				Faint.	Strong.	Trace.
Indications of caramel by paraldehyde.	Slight turbidity.	No turbidity.	Marked turbidity.	Strong.	None.	Strong.
Conclusion as to character of sample.	Artificial.	Genuine.	Artificial.	Mixed whisky 1:4.	Straight whisky.	Not a whisky.

TABLE I.—*Analytical results obtained by cooperating chemists on the referee's samples of whisky.* (*Results calculated to uniform basis of expression*)—Continued.

Determination.	Name of analyst.					
	A. Lasché.			Leroy M. Law.		
	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 1.	Sample No. 2.	Sample No. 3.
Specific gravity, at 15½° C.				0.93020	0.93460	0.93029
Solids (extract):						
Per cent total solids (extract).	0.2896	0.1713	0.1091	.302	.172	.114
Per cent water soluble residue.	.2680	.1285	.1071			
Per cent reducing bodies (dextrose).	.162	.047	.055	.141	.043	.040
Mineral constituents:						
Per cent ash						
Alkalinity of ash (cc N/10 per 100 cc).						
Per cent chlorids						
Per cent sulphates						
Alcohol:						
Per cent alcohol by volume.	52.29	49.89	51.62	52.86	50.61	52.41
Per cent alcohol by weight.				45.18	43.03	44.75
Apparent proof (from gravity).	104.00	99.25	103.00	104.22	99.86	104.12
Real proof	104.58	99.78	103.24	105.72	101.22	104.82
Acids:						
Free acids (cc N/10 per 100 cc).						
Combined acids (cc N/10 per 100 cc).						
Per cent fusel oil	.28	.35	.309			
Color:						
Degree of color (one-fourth inch cell, brewer's scale).				6.0	5.5	6.5
Per cent color removed by ether.	10.75	34.8	7.6	25.0	45.4	8.3
Per cent color removed by fuller's earth.	81.90	61.10	86.90	75.00	54.50	76.90
Qualitative tests, etc.:						
Color				Good.	Good.	Good.
Taste						
Odor				Fair.	Good.	Not like whisky.
Furfurol reaction (per cent).	.008	.01	No reaction.			
Aldehydes	.003	.004	.001			
Indications of tannins by ferric salts.				Moderate.	Strong.	None.
Indications of tannins by lead subacetate.				Moderate.	Strong.	None.
Indications of caramel by paraldehyde.	Turbid.	Negative.	Very turbid.	Yes.	No.	Yes.
Conclusion as to character of sample.	Rectified.	Genuine.	Artificial.	Mixed.	Genuine.	Artificial.

TABLE I.—*Analytical results obtained by cooperating chemists on the referee's samples of whisky.* (*Results calculated to uniform basis of expression*)—Continued.

Determination.	Name of analyst.					
	Harris E. Sawyer.			McCandless, Williams, and Burton.		
	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 1.	Sample No. 2.	Sample No. 3.
Specific gravity, at 15½° C.	0.93144	0.93551	0.93083	.....	.....	.....
Solids (extract):						
Per cent total solids (extract).	.294	.169	.111	0.281	0.169	0.113
Per cent water soluble residue.	.187	.136	.106	.....	.....	.....
Per cent reducing bodies (dextrose).	.095	.044	.036	.....	.....	.....
Mineral constituents:						
Per cent ash	.....	.....	.....	.....	.....	.....
Alkalinity of ash (cc N/10 per 100 cc).	.....	.....	.....	.....	.....	.....
Per cent chlorids	.....	.....	.....	.....	.....	.....
Per cent sulphates	.....	.....	.....	.....	.....	.....
Alcohol:						
Per cent alcohol by volume.	51.50	49.40	51.70	52.02	50.52	52.26
Per cent alcohol by weight.	.....	.....	.....	44.38	42.95	44.60
Apparent proof (from gravity).	103.0	98.8	103.4	.....	.....	.....
Real proof	.....	.....	.....	104.04	101.04	104.52
Acids:						
Free acids (cc N/10 per 100 cc).	5.1	12.4	1.5	*a* .0116	*a* .0298	*a* .0012
Combined acids (cc N/10 per 100 cc).	13.5	15.0	5.7	*b* .0397	*b* .0554	*b* .0255
Per cent fusel oil	.....	.....	.....	*c* .0397	*c* .108	*c* .034
Color:						
Degree of color (one-fourth inch cell, brewer's scale).	.....	.....	.....	.....	.....	.....
Per cent color removed by ether.	12.0	40.0	None.	.....	.....	.....
Per cent color removed by fuller's earth.	75.00	57.00	80.00	80.00	60.0	.....
Qualitative tests, etc.:						
Color	.....	.....	.....	.....	.....	.....
Taste	.....	.....	.....	.....	.....	.....
Odor	.....	.....	.....	.....	.....	.....
Furfurol reaction (per cent).	Moderate.	Strong.	None.	.....	.....	.....
Aldehydes	Moderate.	Strong.	Weak.	.....	.....	.....
Indications of tannins by ferric salts.	Faint.	Strong.	None.	.....	.....	.....
Indications of tannins by lead subacetate.	Slight turbidity.	Strong turbidity.	No change.	.....	.....	.....
Indications of caramel by paraldehyde.	Opalescent.	No change.	Opalescent.	Cloudy.	Clear.	Cloudy.
Conclusion as to character of sample.	Rectified.	Genuine.	Entirely factitious.	Not genuine.	Genuine.	Not genuine.

a Per cent acetic. *b* Per cent ethyl acetate. *c* Per cent amyl alcohol.

Table II shows the average of the analytical figures obtained for extract, alcohol, color removed by ether and by fuller's earth, together with the maximum variation above and below the average figure in each determination.

TABLE II.—*Average, maximum, and minimum results obtained by chemists on referee's samples of whisky.*

	Extract.			Alcohol by weight.			Color removed by ether.			Color removed by fuller's earth.		
	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 1.	Sample No. 2.	Sample No. 3.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Average	0.289	0.169	0.115	44.51	42.57	44.40	13.9	37.8	6.6	75.3	54.8	81.6
Highest variation	.013	.003	.020	.67	.46	.40	11.1	7.6	4.0	6.6	11.2	5.3
Lowest variation	.009	.005	.009	.13	.75	.96	5.9	6.8	6.6	15.3	24.7	4.7

The following results on the estimation of caramel in whisky by the fuller's earth and ether extract methods were obtained by J. A. Le Clerc and C. W. Harrison, of the Division of Foods of the Bureau of Chemistry, and are submitted independently, as they were received too late to be tabulated with the other reports:

TABLE III.—*Estimation of caramel in whisky (Le Clerc and Harrison).*

Sample. No.	Analyst.	Fuller's earth.		Ether extraction.	
		Colorimeter.	Nessler tubes.	Colorimeter.	Nessler tubes.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
1	Harrison	.....	80.0	11.4	7.2
	Le Clerc	76.4	80.5	5.5	9.2
2	Harrison	.....	58.0	21.1	.....
	Le Clerc	59.4	55.0	25.5	19.7
3	Harrison	74.6	.....	.....	.....
	Le Clerc	78.0	.....	4.3	.....

COMMENTS BY ANALYSTS.

H. E. Barnard.—For the extraction of color by ether I employed a Bromwell fusel oil apparatus, and because of the small size of the bulb was obliged to use such a quantity as would bring the separation mark within the scale. This quantity was 22.18 cc for the first sample, 22.45 cc for the second sample, and 22.96 cc for the third sample. In reading the color a corresponding quantity of the 25 cc reserved for treatment on the water bath was used. While it is probable that a small error is introduced by departing from your directions, the results obtained are comparable, and therefore of value.

The depth of color of the extracted liquor was so great that I varied the method by employing but 10 cc instead of 50 cc, as directed, and by taking aliquot parts of the extracted sample when reading the colors. These modifications made it easier to read the colors and the results were the same as when read directly.

It may be noted that while samples 1 and 3 on evaporation gave a sirupy residue of even consistency, sample 2 precipitated out, leaving a residue much harder to take up with water than was the case with the other samples.

Edward Gudeman.—Specific gravity was calculated to 15.5° C, using correction for temperature as given by Allen.[a] The specific gravity of alcohol-free whisky was also determined and the same correction applied. From these two gravities the percentage of alcohol was calculated, using the table in Bulletin No. 65, page 121. No direct alcohol determination was made, the results being used only for calculation purposes.

[a] Commercial Organic Analysis, *1:* 93.

Preference is given to this method where accurate results are not required, as the solution after boiling off the alcohol and making up to original bulk can be used for the ether extraction. I place great reliance as to the quality of the whisky on the appearance of this alcohol-free product. I take notice of the appearance as to cloudiness and change in color and separation of any oily or resinous material.

For ether extract: Evaporate on water bath 100 cc of whisky to 25 cc, make to original bulk, and evaporate to 50 cc; make to original bulk, cool, take specific gravity. Shake out with 50 cc of ether twice. Use centrifugal machine if separation is not good. Observe color of ether extract, evaporate to small bulk on water bath and to dryness spontaneously. Residue can be weighed after drying over sulphuric acid for 48 to 72 hours. Observe color of residue, character as to being resinous and oily, and take notice of bouquet. Straight whiskies aged in wood will be resinous, oily, and have strong bouquet. Quantity of extract residue I do not consider of any value, as same depends on method of purification in manufacture and time of aging.

I place also great reliance in the lead subacetate precipitate. Observe time of formation and approximate amount of precipitate compared with total volume of solution, also manner of settling of precipitate and color. I use 10 cc of whisky to 1 cc of subacetate. Take notice of amount of precipitate formed in 10 minutes and amount of precipitate formed in 16 hours' standing without agitation of any kind. The precipitate from straight whiskies will be gelatinous and not settle to more than one-fourth of the bulk in 16 hours. Compounded whiskies and mixed whiskies will settle quicker and the precipitate be firmer—in fact, the amount of precipitate after 16 hours is an indication of the character of the whisky and gives an approximate clue to the amount of mixture.

I modify the paraldehyde test slightly, making the whiskies of an alcohol strength between 40 and 45 per cent by weight. Use 20 cc of this whisky, 80 cc of paraldehyde, and 20 cc of 95 per cent alcohol, and allow to stand for 16 hours (over night). Note the color and amount of precipitate formed and test its reducing power, after purifying by washing with 95 per cent alcohol.

The fuller's earth test I make on whisky reduced or increased to same alcohol strength as for aldehyde test. Use 25 cc of whisky and 5 grams of fuller's earth. Shake every 5 to 7 minutes for 1 hour, allow to stand for 1 hour, and then filter through an S. & S. wet filter. Use the same solution for direct polarization. Keep the test tubes corked to prevent evaporation. The amount of color taken out is only approximated and not measured with a tintometer.

The percentage of alcohol determined by specific gravity is sufficiently accurate to prepare the 40 to 45 per cent alcohol solution used in these two tests.

Total solids and ash are determined exactly as in vinegar analyses, evaporating on boiling-water bath for 1 hour.

Alkalinity of ash is determined by dissolving the ash from 100 cc in N/10 sulphuric acid and titrating back excess of acid used, using phenolphthalein as indicator.

Sulphates and chlorids are tested for in the original whisky, and if found the ash is tested for same. Results found on the ash are taken into consideration.

I place great reliance on the test for tannic acid. No pure, aged-in-wood whisky is free from tannic acid, and it will give a strong characteristic reaction. I test the whisky direct and the alcohol-free whisky.

In cases where the solution from the fuller's earth test is too highly colored for the polarization, use the subacetate filtrate, allowing 10 per cent for the subacetate, but make no correction for bulk of precipitate. If polarization is not over 0.1 either way I make no examinations for sugars. If polarization is more, I examine for reducing sugars and make the polarization test before and after inversion. This test is only considered necessary if total solids are relatively high.

A. Lasché.—The chloroform absorption test was used as follows: If to 5 cc of whisky contained in a test tube 5 cc of chloroform are added and then an addition of 10 cc of

water made and the mixture shaken carefully once or twice, avoiding an emulsion, the chloroform will absorb the color of the aqueous layer, leaving the aqueous layer colorless. (*Straight whisky.*) If caramel is the coloring of a whisky, the chloroform layer will remain absolutely colorless, while the aqueous layer will remain *colored.* If caramel was used to reinforce the color of whisky, both layers will be colored. The samples submitted were subjected to the above test, with the following results: No. 1, both layers are colored; No. 2, the aqueous layer is colorless; the chloroform layer absorbed all of the color; No. 3, the chloroform layer is *entirely colorless.*

H. E. Sawyer.—The reducing bodies of the soluble extract were determined by adding the latter to 50 cc of freshly mixed copper reagent, diluting to 100 cc, boiling for 2 minutes, weighing (cuprous oxid), and calculating as invert sugar.

Tenth normal potassium hydrate was used for the titrations, no barium hydrate being on hand. The alkali was free of carbonates. The esters were saponified by adding excess of alkali, and leaving for 5 days at temperature of room.

It was not practicable to make an accurate estimation of either the furfurol or the total aldehydes. It was readily seen, however, that both were present most abundantly in the genuine sample.

The amounts of color removed by ether and fuller's earth were estimated carefully, rather than determined accurately, since the writer has no colorimeter adapted to this work.

The paraldehyde test gave no results of any significance.

In addition to the preceding determinations, a number of qualitative tests were applied to the samples; and in some cases marked differences of reaction were observed. The following are worthy of mention:

Ferric alum test for tannin: Three or four drops of a 1 per cent solution were added to about 5 cc of each sample. No. 3 remained unchanged; No. 1 turned greenish, and No. 2 turned a very dark blackish-green.

Lead subacetate test for tannin: Two or three drops reagent, to about 5 cc of sample. No change in No. 3; slight turbidity in No. 1; heavy brown turbidity in No. 2.

Molisch a-naphthol test for carbohydrates:[a] No. 1 reacts; Nos. 2 and 3 give a brown ring quite different from No. 1.

Cobalt nitrate test for sucrose:[b] No. 1 gives faint sucrose reaction; No. 2 does not; No. 3 was not tested.

The tests with ferric alum, naphthol, and cobalt nitrate deserve the attention of the referee during the coming year. Genuine liquors are characterized by a reaction for tannin, more or less strong, according to the time they have remained in casks. Also, it is well recognized that a certain amount of sugar is commonly added to "rectified" liquors to give them body and smoothness.

These tests, with others not reported here, are being studied in the writer's laboratory on a large number of samples of known origin, in the hope of determining their limits of sensibility and of elaborating them into reliable quantitative colorimetric determinations.

John M. McCandless.—As to the methods of analysis, alcohol was determined in the usual way, coloring matter was determined by Crampton and Simons's method, with fuller's earth, and the results in each case confirmed by the paraldehyde test. We find both of these tests valuable and confirmatory of the conclusions reached from other determinations.

For the determination of acidity as acetic acid, ethers as ethyl acetate, and fusel oil as amyl alcohol, the excellent method given in the third edition of Allen's Commercial Organic Analysis[c] was followed. Only a moderate quantity of the liquor is

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[a] Mulliken, Identification of Pure Organic Compounds, p. 26.

[b] Wiley, Principles and Practice of Agricultural Analysis, *3*: 189. For "five cubic centimeters," p. 189, line 17, § 167, read one-half cc.

[c] Vol. 1, p. 154.

required, 100–200 cc, and from this portion the acidity, the ethers, and the fusel oil are all obtained, and, according to our belief and experience, with greater ease and accuracy than by the use of association methods and of the Bromwell apparatus method. Allen, in speaking of the method, says it "is a great improvement on that prescribed by Marquardt. It substitutes a rapid, easy, and delicate titration for a treatment with barium carbonate (and chance of imperfect neutralization), followed by filtration, evaporation, drying, weighing, and supplementary determinations of barium and chlorin." Furthermore, it enables an analyst after completing the determination to calculate the combining weight of the organic acid resulting from the oxidation of the higher alcohols by the chromic acid mixture, and therefore to infer its identity with valeric acid, and also to obtain from the final residue the characteristic odor of valeric acid. We hope that this method may be given a careful trial in the work of another year. It is also obvious from an inspection of the table that the figures for acidity, for ethers, and for fusel oil are very valuable criteria in judging of the purity of a liquor and in helping us to draw a probable inference as to whether a whisky is wholly factitious or has had some genuine whisky added to it.

J. A. Le Clerc and C. W. Harrison.—From the appearance of the liquid after treatment with fuller's earth, and from the amount of coloring matter removed, we concluded that No. 1 was an adulterated or factitious whisky. No. 2 was genuine. No. 3 was made in the laboratory. The appearance of No. 3, after treatment with fuller's earth, was a pale straw color, decidedly of a different tint from the original, so different, in fact, that it was with difficulty that we could estimate the per cent of color removed. In this case it was impossible for us to obtain any concordant results, using Nessler tubes. The flavor of No. 3 was also more like that of vanilla than of a true whisky.

Comments of Associate Referee.

The result of the cooperative work upon distilled liquors is quite satisfactory, as every analyst was able to arrive at correct conclusions concerning the character of the samples by the use of determinations and tests now incorporated in the methods of the association. The primary object of the associate referee in sending out the samples was to determine the sufficiency of the association methods to this end.

In addition, the work has brought out a number of new or proposed tests which promise to afford additional means for the identification of adulterated liquors. Some of these have been examined in this laboratory, and a partial report might be made upon them here, but it is thought best, on the whole, to refer all over to another year, so that a more careful study may be made.

Of the methods recommended for this year's work, the returns show that the modified paraldehyde test has proved very valuable. The methods for the detection of caramel coloring have also demonstrated their value.

It is true the percentage results obtained by different analysts vary greatly on the same samples; but when it is considered that none of the analysts used colorimeters to measure the color of their solutions, and but one or two used the special form of apparatus recommended for the ether extraction, it is remarkable that they agree as well as they do. From the nature of these tests, it is apparent that different analysts would be obliged to observe very rigid and uniform conditions to obtain percentage results that would be at all comparable. But this is not at all essential to the efficiency of the tests; an analyst may erect his own standards, and by operating under uniform conditions upon genuine and suspected samples he can readily obtain results which will enable him to discriminate between the two classes of liquors. All the analysts found wide differences in the behavior of natural and artificially colored spirits toward ether and fuller's earth. However it is very desirable that a test should give figures that agree in the hands of different analysts, and it would seem that the ether absorption test, particularly, is capable of giving uniform results by closer adherence to a prescribed method of procedure and a careful measure of color.

It was not intended this year to make a very careful study of the quantitative determinations, such as extract and alcohol, with a view to testing the methods prescribed for these estimations; however, the returns show a very good agreement on the determination of extract, the maximum variation above the average being 0.02 per cent and the maximum below being 0.009 per cent.

The alcohol results are by no means so satisfactory. This is perhaps the fault of the writer in sending out instructions to the effect that this determination was unimportant, yet while the content of alcohol is of little importance in determining the question of the genuineness of a whisky, it is nevertheless the most important estimation, commercially, in the analysis of distilled spirits, and may be made with considerable accuracy. This being true, a variation of 0.67 per cent above and of 0.96 per cent below the average is entirely too wide a range of results. Internal-revenue gaugers get closer results with a hydrometer. The principal cause is probably a loss of alcohol during distillation, and the careful weighing, instead of measuring, of samples and distillates would doubtless also contribute greatly toward accuracy.

Only two of the analysts made a determination of fusel oil, but these two results (which are hardly within hailing distance of one another on identical samples) show the crying need of greater uniformity of method and execution in the estimation of this important constituent, or rather group of constituents. Attention was called to this need in last year's recommendations. Two of the collaborators volunteered to undertake a comparison of methods this year, but were unable to fulfill their promises on account of a pressure of work, and the same cause prevented anything being accomplished in that direction in the referee's laboratory. It is difficult for a busy chemist to persuade himself that the time and care required for the estimation afford any adequate return in the results obtained, which seem to give little information concerning the character of the spirits under consideration. Yet the estimation is considered a very important one, and is used in Germany as an analytical standard.

It is hoped that the increasing attention which is being devoted to the composition of distilled liquors will soon result in a better knowledge of the numerous and various substances now included under the designation of fusel oil constituents. Even a study and comparison of existing methods involves so much time and labor that it is almost out of the question for any but a chemist with time and means for research work at his disposal.

Literature.

The principal addition to the literature of this subject during the past year is a new method for the quantitative determination of fusel oil, of which the following is an abstract:

Quantitative determination of fusel oil—isoamyl alcohol—in rectified spirits, by means of salicylic aldehyde.[a]

This method is the result of the development of Saglier's qualitative test of the presence of isoamyl alcohol in rectified spirits by means of the coloration produced by sulphuric acid in the presence of furfurol. By this test a dilute alcoholic solution of furfurol is mixed with the spirit, and concentrated sulphuric acid then added. Isoamyl alcohol is indicated by a more or less intense rose-red coloration.

In experimenting with this test it was found that salicylic aldehyde could be used in place of the furfurol (though it is not so sensitive) and indeed with better results, since the furfurol coloration was found not to be uniform. The salicylic aldehyde reaction has lately been further studied with a view of making it quantitative, and the method at present is as follows: To 10 cc of spirit and 10 cc each of standard solution containing from one to nine parts of isoamyl alcohol in alcohol, 25 to 30 drops of sali-

[a] Dr. A. Komorowski, in Chemiker Zeitung, 1903, No. 66, p. 807, and No. 88, p. 1086.

cylic aldehyde solution (1:100 of alcohol) and 20 cc of concentrated sulphuric acid are added.

The tests are shaken and compared when cool. Acetaldehyde increases the intensity of color, and therefore must be estimated and correction made by means of another set of standards similar to the above, but containing in addition different amounts of acetaldehyde.

REPORT ON BAKING POWDER AND BAKING CHEMICALS.

By R. O. Brooks, *Associate Referee.*

As associate referee on baking powder and baking chemicals for the year 1904, I submit the following summary of results obtained in the study of the provisional official methods of analysis, as outlined in Bulletin 65, Bureau of Chemistry, United States Department of Agriculture, pages 98 to 107.

Upon receipt of the list of collaborators in baking powder work, early in the spring, a circular letter, outlining and suggesting several different lines of investigation, was sent to each of the names furnished, twenty-one in all. Several acknowledged the receipt of this circular letter, but as yet no one has reported on work done; hence the following summary deals only with work undertaken by the writer.

As the circular letter stated, the special aim of the season's work was to ascertain what determinations are sufficient for the rapid inspection analysis of leavening chemicals, and at the same time accurate enough for court evidence purposes; and to compare several old and new methods for the analysis of cream of tartar powders and alum and phosphate powders with the provisional methods, keeping the first point in mind meanwhile.

A comparison of several of the simple alkalimeters which will stand gentle boiling over asbestos (Schroetter's, for example) with the somewhat elaborate Knorr or Heidenhain apparatus, for the carbon dioxid determinations, was suggested. The writer, using a Schroetter alkalimeter, obtained almost theoretical results with known weights of sodium bicarbonate, by very gently boiling after the action of the acid had ceased and carefully aspirating to remove all carbon dioxid from the apparatus.

As the Goldenberg-Geromont-Heidenhain method for total tartaric acid is rather long and not adapted to powders (or cream of tartar itself) containing alum, phosphates, etc., a thorough trial of the new polariscopic method devised by the Kenrick brothers, and first announced in the appendix to Bulletin 65, was suggested. The writer found that, in every conceivable mixture of cream of tartar and its usual adulterants and of cream of tartar and tartaric acid, singly and together, in baking powders, the amounts of tartaric acid found by means of the polariscope and those taken for analysis agreed very closely. The possibility of getting practically theoretical results is dependent only upon the ability of the analyst to make a correct polariscopic reading, and for simplicity, neatness, and rapidity the method is all that could be desired.

To avoid the very tedious potash determination given in Bulletin 65 for powders containing both cream of tartar and tartaric acid, or cream of tartar alone, the writer worked out and outlined for trial in the above-mentioned circular letter an entirely new, simple, and very rapid method of analysis, utilizing principally carbon dioxid determinations before and after fusion on two separate portions of the sample. Thus, in a sample containing both cream of tartar and free tartaric acid, the combined tartaric acid was calculated from the results of (*a*) the determination of total alkalinity in the completely fused powder by titration with decinormal sulphuric acid, and (*b*) the determination of carbon dioxid in the original powder by use of Knorr's or a similar satisfactory apparatus when estimating the proportion of bicarbonate present. The amount of carbon dioxid corresponding to the total alkalinity

of the fused powder minus that found in the bicarbonate estimation equals that corresponding to the potassium bitartrate (cream of tartar) present. From the amount of the bitartrate thus found and the total tartaric acid, determined by the polariscope preferably, the quantity of free tartaric acid present can readily be calculated. If cream of tartar alone be present, the polariscopic method is useful as a check upon the fusion method, given above, of estimating bitartrate and bicarbonate simultaneously. More complete details and several experiments showing the accuracy of this method of the writer's can be found in the Journal of the American Chemical Society for July, 1904.

In connection with the above work the writer had occasion to test extensively the several qualitative tests for free and combined tartaric acid, given in the provisional methods of analysis. The test for free tartaric acid, depending upon the solubility of the free acid in absolute alcohol and the insolubility of the bitartrate, worked very satisfactorily, there being no extracted matter giving a silver mirror when warmed with dilute ammonia and a crystal of silver nitrate from a powder containing no free tartaric acid. From a powder containing less than 0.5 per cent of free tartaric acid, however, an extract giving a pronounced test was obtained. The so-called Wolff test (Bulletin 65, p. 104) for tartaric acid, either free or combined, in which 5 grams of the sample are shaken with 250 cc of water for some time, filtered, the filtrate evaporated to dryness, a few drops of 1 per cent resorcinol solution and 3 cc of strong sulphuric acid added and the mixture heated slowly with the development of a supposedly characteristic rose-red color when tartaric acid is present, proved to be very unsatisfactory in the writer's hands. Practically, every usual adulterant of cream of tartar, or baking powder containing such, gave a similar color, or one easily confused with it, by the above test, when absolutely no tartaric acid, either free or combined, was present.

The writer has always found the simple method of shaking a little of the sample with 10 per cent ammonia water, filtering, adding a crystal of silver nitrate and warming (with the appearance of a silver mirror if free or combined tartaric acid be present) very satisfactory. No cream of tartar adulterant or substitute or any other usual ingredient of baking powders gave the least trace of a mirror by this test, and it is of course much quicker than any test involving the evaporation of a large volume of water, as does the Wolff test. The use of this simple test upon a portion of the sample for tartaric acid generally (free or combined) and the similar testing of the alcoholic extract from another portion for free tartaric acid, leaves nothing to be desired along the line of qualitative tartartic acid tests in baking-powder analysis.

The last line of investigation suggested in the circular letter was a comparison of the K. P. McElroy method[a] for alum and phosphate determinations in alum-phosphate powders, with the methods given in Bulletin 65. A possible argument in favor of the former method is that the two determinations are made upon one portion of the sample; the aluminum being precipitated with ammonia in the filtrate from the phosphomolybdate precipitation, whereas in the provisional methods one portion of the sample is used for a phosphate determination (closely resembling that outlined by McElroy) and another portion used for a determination of aluminum as aluminum phosphate. Working with an alum-phosphate powder containing chemically pure acid calcium phosphate ($H_4Ca\ (PO_4)_2$), the writer obtained practically theoretical results in the phosphate determinations. Using chemically pure uneffloresced crystals of ammonia alum in the preparation of the above alum-phosphate powder, two determinations as aluminum phosphate gave results each exactly 2.6 per cent too high. One determination, by precipitation with ammonia as in McElroy's method, gave a result 6.6 per cent above the theoretical. The separate aluminum determination (as aluminum phosphate) as outlined in Bulletin 65, thus appears to be the more

[a] Leffmann and Beam, Food Analysis, p. 112.

accurate, but further study is apparently needed along this line before a decision can be reached[a].

REPORT ON TEA AND COFFEE.

By Hermann C. Lythgoe, *Associate Referee.*

I. Tea.

The adulteration of tea consists largely in the substitution of inferior for superior grades, and the detection of this falsification concerns the tea taster. Other forms of adulteration are the addition of tea stems and dust, and the facing of tea to improve its appearance. The presence of foreign leaves is so rare that it is generally useless to look for them.

METHODS.

1. *Detection of stems, dust, and foreign leaves.*

Place 1 gram of tea in a 300 cc casserole, add 200 cc of water and boil for 15 minutes. This treatment will cause the leaves to unroll and a megascopic examination will reveal the presence or absence of stems or dust, while the leaves will be in condition for examination as to their form and structure.

2. *Detection of facing.*

Tea is faced by treating with mineral pigments, graphite, catechu, etc. Mineral pigments can be detected in the ash, or the tea may be shaken up with a large volume of water, and the water separated from the leaves by a sieve, when the insoluble mineral substances used in facing will settle, and can be removed by filtration for further examination, the catechu and other soluble substances being in the filtrate.

3. *Chemical analysis.*

The sample should be ground fine enough to pass through a 40-mesh sieve. Determine the moisture, ash, soluble ash, sand, alkalinity of the ash, phosphates, petroleum ether extract, crude fiber, and nitrogen, as described under coffee.

4. *Water extract.*

Method of Krauch.[b]—Treat 20 grams of tea with 400 cc of water and heat on a boiling water bath for six hours. Filter through a tared filter, wash with water until the filtrate measures 1,000 cc, dry and weigh the residue. The water-soluble substance is determined by difference.

5. *Volatile oil.*

Distill 100 grams of tea with 800 cc of water, extract the filtrate several times with petroleum ether, evaporate the combined petroleum ether extracts at the room temperature, dry in a desiccator and weigh.

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[a] After completing this report a letter was received from C. W. Nelson, of the food laboratory, Bureau of Chemistry, giving a comparison of the Schroetter alkalimeter and Heidenhain's carbon dioxid apparatus, and also of the referee's method for bitartrate in a cream of tartar powder and the provisional method for total tartaric acid. The differences between the two kinds of carbon dioxid determinations are all within the limits of experimental error and are not the same in either method throughout. Two of the three sets of bitartrate determinations agree moderately well. The third set shows a difference of about 4.6 per cent, the provisional method giving the lower result.

[b] König, Zts. Nahr. Genussm., 3d edition, p. 1057.

6. *Determination of theine.*

Method of P. Dvorkowitsch.[a]—Digest 10 grams of the powdered tea with 200 cc of boiling water for five minutes, and decant the solution; repeat the treatment twice and boil the residue twice with 200 cc of water. Make up the combined solutions to 1,000 cc and extract a portion with petroleum ether to remove the fat, etc. To 600 cc of the fat-free solution (equivalent to 6 grams of tea) add 100 cc of 4 per cent barium hydroxid, mix and filter. To 583 cc of the filtrate (equivalent to 5 grams of tea) add 100 cc of a 20 per cent solution of sodium chlorid, and extract three times with chloroform. Distill the majority of the chloroform from the combined extracts, place the residue in a tared dish, evaporate the remainder of the chloroform, dry at 100° and weigh. The theine is usually of sufficient purity to render a nitrogen determination unnecessary.

7. *Determination of tannin.*

Procter's modification of Löwenthal's method.[b]—Reagents: (1) Potassium permanganate solution containing about 1.33 grams per liter.

(2) Tenth normal oxalic acid solution (6.3 grams per liter).

(3) Indigo carmine solution, containing 6 grams indigo carmine (free from indigo blue) and 50 cc concentrated sulphuric acid per liter.

(4) Gelatin solution, prepared by soaking 25 grams of gelatin for one hour in a saturated sodium chlorid solution, heating until the gelatin is dissolved, and making up to 1 liter after cooling.

(5) Mixture of 975 cc saturated sodium chlorid solution and 25 cc concentrated sulphuric acid.

(6) Powdered kaolin.

Obtain the value of the potassium permanganate in terms of the oxalic acid.

Boil 5 grams of the tea for half an hour with 400 cc of water; cool, transfer to a graduated 500 cc flask and make up to the mark. To 10 cc of the infusion (filtered if not clear) add 25 cc of the indigo carmine solution and about 750 cc of water. Then add from a burette the potassium permanganate solution, a little at a time while stirring, till the color becomes light green, then cautiously, drop by drop, until the color changes to bright yellow or further to a faint pink at the rim. The number of cubic centimeters of permanganate used furnishes the value a of the formula.

Mix 100 cc of the clear infusion of tea with 50 cc of gelatin solution, 100 cc of salt acid solution, and 10 grams of kaolin, and shake several minutes in a corked flask. After settling, decant first the clear supernatant liquid through a filter and finally bring the precipitate upon the filter. Mix 25 cc of the filtrate (corresponding to 10 cc of the original infusion) with 25 cc of the indigo solution and about 750 cc of water, and titrate with permanganate as before. The number of cubic centimeters of permanganate used gives the value b, $a-b=c$, c=permanganate required to oxidize the tannin. Assume that 0.04157 gram tannin (gallotannic acid) is equivalent to 0.063 gram oxalic acid.

II. Coffee.

The analysis of coffee for the detection of adulteration is largely microscopical, but a chemical examination is often of advantage to supplement the microscopical examination and to assist in arriving at the approximate percentage of the adulterants.

The adulterants of coffee are probably more diversified than those of any other food. In roasted coffee there have been found roasted cereals and legumes of all varieties, roasted chicory and other sweet roots, and in short nearly everything that when roasted possesses a dark color and an aroma somewhat suggestive of coffee. Perhaps the most common form of adulteration is the substitution of inferior for superior grades, but unfortunately it is not possible at present to distinguish between different grades of coffee by chemical tests.

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[a] Ibid., 4th edition, p. 1010.

[b] U. S. Dept. of Agr., Division of Chemistry, Bul. 13, Part 7, p. 890.

METHODS.

A. *Raw coffee.*

Raw coffee is sometimes treated with water to increase its weight. This form of adulteration can be detected by drying 5 grams of the ground coffee at 100° for three hours. The amount of moisture in raw coffee is from 9 to 13 per cent.

The inferior grades are sometimes colored to imitate the better grades. Such pigments as ocher, litharge, lead chromate, and chromic oxid, such organic colors as indigo, turmeric, azo yellow, malachite green, methyl green, etc., have been used for this purpose. The mineral colors can be identified in the ash or removed from the bean by shaking with water, in which case the soluble colors can be identified in the solution and the insoluble ones in the residue.

B. *Roasted coffee.*

1. Examination of the Whole Beans.

Examine the sample megascopically in order to detect foreign substances. Artificial coffee beans are apparent from their exact regularity of form; coffee pellets are made from roasted wheat mash and are of a brown color, possessing a very characteristic ellipsoidal form; roasted legumes and lumps of chicory are sometimes present and are easily identified by the practiced eye. Coffee is glazed by treating the raw beans with molasses, sugar solution, glycerin, or fats and waxes, and then roasting.

2. Detection of Sugar Glazing.

Method of Stutzer & Reitnair.[a]—Twenty grams of the whole beans are treated with 500 cc of water in a liter flask and shaken vigorously for five minutes. Complete the volume to the mark with water, mix, filter, and determine the solids and ash in 50 cc of the filtrate. The difference between these two figures gives the soluble organic matter, which, in unglazed coffee, is from 0.44 to 0.72 per cent, and in glazed coffee from 1.81 to 8.18 per cent.

3. Detection of Glycerin.

Proceed as directed under wines[b] on a portion of the filtrate from 2.

4. Detection of Fats and Waxes.

Method of E. Späth.[c]—Treat 100 to 200 grams of the beans with low boiling petroleum ether for ten minutes, pour off the petroleum, and repeat the process. Filter the combined petroleum ether extracts, evaporate the solvent, and determine the saponification number and index of refraction of the residue.

C. *Physical Examination of Commercial Ground Coffee.*

5. Megascopic Examination.

The practiced analyst can tell at a glance if there is any appreciable amount of adulteration. Roasted grains possess a glossy appearance entirely foreign to that of roasted coffee, and if roasted legumes are present, fragments of the hulls can be seen.

6. Microscopic Examination.

Grind a portion of the sample in a porcelain mortar to the requisite degree of fineness, which one soon learns by experience, place a portion on a microscope slide, add a drop of water, place a cover glass on the specimen, and rub out between the thumb and finger. Too much rubbing or grinding is to be avoided, as the characteristic microscopical appearance of the cell structure of the coffee will be destroyed. Examine with a $\frac{1}{6}$-inch objective and a 1-inch ocular.

With pure coffee one sees fragments of the hexagonal cells, and the oil drops. Roasted grains are apparent from the starch grains which, though somewhat distorted by the roasting, can be easily identified. Roasted legumes show the starch

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[a] Pharm. Centralh., *22*: 134.
[b] U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, p. 82.
[c] Forschungsberichte über Lebensmittel, 1895, *2*: 223.

granules, and in a striking manner, the hulls resembling bunches of matches. When roasted chicory is present, the cellular tissue is apparent and also fragments of the juice ducts. For photomicrographs of these substances see the Massachusetts State Board of Health, Annual Report for 1900, Plate VI, figs. 21, 22, 23, 24, Leach. "Food Inspection and Analysis." John Wiley & Sons. Plate XIV, figs. 173, 174, 175, 176; Plate XV, figs. 177, 178, 179, 180; Plate XVI, figs. 181, 182, 183.

D. *Chemical Examination of Coffee.*

7. Preparation of the Sample.

Grind until the sample will pass through a forty-mesh sieve.

8. Moisture.

Place 5 grams of the sample in a flat-bottomed platinum dish and dry for three hours in an oven at 100°, cool in a desiccator, and weigh. The loss is moisture.

9. Total Ash.

Burn the dry residue from the above treatment in a muffle, cool, and weigh.

10. Water Soluble Ash.

Boil the ash as obtained above in 50 cc of water, filter through an ashless filter, wash with boiling water, place the filter in the platinum dish, ignite, and weigh. The difference between this weight and that of the total ash gives the weight of the soluble ash.

11. Ash Insoluble in Acid, or Sand.

Boil the ash insoluble in water with 50 cc of 10 per cent hydrochloric acid, filter on an ashless filter paper, wash with water, ignite, and weigh.

12. Chlorin.

Treat the water solution of the ash (filtrate of 10) with an excess of dilute sulphuric acid, add a slight excess of magnesia, and titrate with tenth normal silver nitrate, using potassium chromate as an indicator. (This determination is useful if chicory be present, and also to determine if sea water has been used as a make-weight in raw coffee.)

13. Alkalinity of the Ash.

Weigh 10 grams of the coffee in a platinum dish and burn to an ash in a muffle, boil the ash with 100 cc of water for ten minutes, filter, and wash with water until free from alkali. To the filtrate add from a burette an excess of tenth normal hydrochloric acid, boil to expel the carbonic acid, and determine the excess of acid by titrating with tenth normal alkali, using phenolphthalein as an indicator, express results as cubic centimeters of tenth normal acid required to neutralize the ash of one gram of coffee and also one gram of coffee ash.

14. Soluble Phosphates.

Make the final solution of 13 slightly acid with dilute hydrochloric acid and evaporate to dryness, add 50 cc of boiling water, and titrate in the usual manner with uranium solution.[a]

15. Insoluble Phosphates.

Dissolve the insoluble ash of 13 in dilute hydrochloric acid, evaporate to dryness, add ten drops of dilute hydrochloric acid to the residue, dissolve in 50 cc of boiling water, add 1 gram of sodium acetate, and titrate with uranium solution.

16. Petroleum-Ether Extract.

Dry 2 grams of coffee at 100°, extract with petroleum ether (boiling points from 35° to 50°) for 16 hours, evaporate the solvent, dry the residue at 100°, and weigh.

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[a] Sutton's Volumetric Analysis, 8th ed., p. 313.

17. Total Nitrogen.

Use the regular Gunning method, taking three grams of the sample. This gives the total nitrogen due to both the proteids and the caffeine. To obtain the proteid nitrogen, subtract from the total nitrogen the nitrogen due to caffeine obtained by direct determination on the separated caffeine or by calculation (caffeine÷3.464= nitrogen).

18. Cold Water Extract.

Winton's method.—Place 4 grams of the sample in a 200 cc flask, add water to the mark, and allow to macerate 8 hours with occasional shaking; let stand 16 hours more without shaking, filter, evaporate 50 cc of the filtrate to dryness in a flat-bottomed dish, dry at 100°, and weigh.

19. Reducing Sugars.

Treat 100 cc of the cold water extract obtained in 18 with 0.5 gram of lead acetate, shake until dissolved, add 1 gram of sodium sulphate, shake until dissolved, filter, and determine the reducing sugars in the filtrate. Calculate as dextrose.

20. Cane Sugar.

Take one-half the normal weight for the Schmidt & Haensch polariscope (13.024 grams), place in a 100 cc flask, add water, mix, add 5 cc of lead subacetate, make up to the mark, mix well, and filter. Treat another half normal weight in the same manner in a 200 cc flask. Polarize the two solutions in the 200 mm tube. Invert the two solutions and polarize as usual. The product of the two direct readings divided by their difference,[a] and the quotient multiplied by 2 gives the true direct reading. Obtain the true invert reading in a similar manner and calculate the sucrose by Clerget's formula. (So-called soluble coffee has been found containing as high as 30 per cent of cane sugar.)

21. Copper-Reducing Matter by Acid Conversion.[b]

Use 4 grams of the sample and apply the official method.

22. Copper-Reducing Matter by Diastase.[c]

Use 4 grams of the sample and apply the official method.

23. Crude Fiber.[d]

Use the official method, taking the residue exhausted by the petroleum ether for the sample.

24. Ten Per Cent Extract.

Method of McGill.[e]—Weigh into a tared flask the equivalent of 10 grams of the dried substance, add water until the contents of the flask weigh 110 grams, connect with a reflux condenser and heat, beginning the boiling in from 10 to 15 minutes. Boil for 1 hour, cool 15 minutes, weigh again, making up any loss by the addition of water, filter, and take the specific gravity of the filtrate at 15°.

According to McGill, a 10 per cent extract of pure coffee has a specific gravity of 1.00986 at 15°, and under the same treatment chicory gives an extract with a specific gravity of 1.02821. In mixtures of coffee and chicory the approximate percentage of chicory may be calculated by the following formula:

$$\text{Per cent of chicory} = 100 - \frac{(1.02821 - \text{sp. gr.})\ 100}{0.01835}$$

The index of refraction of the above solution may be taken with the Zeiss immersion refractometer or with the Abbé refractometer.

A 10 per cent coffee extract $n_D\ 20° = 1.3377$.
A 10 per cent chicory extract $n_D\ 20° = 1.3448$.

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[a] Double Dilution Method of Wiley and Ewell, Analyst, *21:* 182.
[b] Bul. 46, p. 25, section (e).
[c] Ibid, section (d).
[d] Ibid, p. 25, section (g).
[e] Transactions of the Royal Society of Canada, 1887.

Determinations of the solids, ash, sugar, nitrogen, etc., may be made on the 10 per cent extract, if desired.

25. Caffeine.

Method of Hilger and Fricke.[a]—Take 5 to 10 grams of coffee, add 100 cc of water and boil, filter, and treat the residue twice more with boiling water. Add to the united filtrates an excess of lead acetate, filter and wash. Treat the filtrate with hydrogen sulphid to remove the excess of lead, filter, wash, and evaporate the filtrate to dryness in a Hoffmeister schälschen with some sand and a little magnesia. Crush the schälschen between filter paper, place in a continuous-extraction apparatus, and extract with chloroform until exhausted. Dry the chloroform extract at 100° and weigh as caffeine. If the caffeine does not appear to be pure, determine the nitrogen in the residue by the Gunning method. N. $\times 3.464$ = caffeine.

26. Caffetannic Acid.

Krug's Method.[b]—Treat 2 grams of the coffee with 10 cc of water and digest for 36 hours, add 25 cc of 90 per cent alcohol and digest 24 hours more, filter and wash with 90 per cent alcohol. The filtrate contains tannin, caffeine, color, and fat. Heat the filtrate to the boiling point and add a saturated solution of lead acetate. If this is carefully done, a caffetannate of lead will be precipitated containing 49 per cent of lead. As soon as the precipitate has become flocculent, collect on a tared filter, wash with 90 per cent alcohol until free from lead, wash with ether, dry, and weigh. The precipitate has the following composition: $Pb_3C_{15}H_{18}O_{82}$. The weight of the precipitate multiplied by 0.51597 gives the weight of the caffetannic acid.

The following results were obtained by the use of these methods:

Table I.—*Analyses of roasted coffee and coffee substitutes.* (*Lythgoe.*)

Variety.		Moisture.	Ash.	Water-soluble ash.	Sand.	Chlorin.	Alkalinity of—		Soluble P_2O_5.	Insoluble P_2O_5.	Petroleum-ether extract.	Index of refraction of extract at 30°.	Total nitrogen.
							Ash of 1 gram of substance.	1 gram of ash.					
		Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*cc n/10 acid.*	*cc n/10 acid.*	*Per ct.*	*Per ct.*	*Per ct.*	$n_{D_{30}}$	*Per ct.*
Santos	A	1.40	4.16	3.46	0.00	0.023	2.97	71.4	0.319	0.346	14.58	1.4754	2.26
	B	1.87	4.31	3.62	.00	.023	3.36	75.7	.286	.295	13.84	1.4754	2.26
	C	1.31	3.80	3.00	.00	.019	3.35	85.6	.273	.295	13.86	1.4750	2.39
Porto Rico	A	1.29	4.05	3.30	.00	.016	3.53	87.2	.305	.337	13.00	1.4752	2.28
	B	1.26	4.06	3.27	.00	.020	3.72	92.6	.226	.351	13.34	1.4750	2.26
	C	1.48	4.12	3.32	.00	.016	3.66	88.8	.333	.328	14.12	1.4760	2.33
Rio	A	1.76	4.06	3.40	.00	.020	4.16	102.3	.213	.166	13.38	1.4758	2.14
	B	2.34	3.91	3.24	.00	.021	3.17	81.2	.356	.227	13.71	1.4753	2.18
	C	2.10	3.74	3.06	.00	.023	3.22	86.6	.363	.236	13.53	1.4756	2.26
Mocha	A	2.05	4.05	3.25	.00	.016	3.94	97.4	.282	.351	14.84	[a]1.4737	2.28
	B	2.95	3.85	3.07	.00	.021	3.26	84.7	.333	.364	14.47	[a]1.4743	2.00
	C	2.40	3.80	3.00	.00	.012	3.54	93.3	.337	.545	15.18	[a]1.4740	2.02
Java	A	3.34	4.09	3.27	.00	.016	3.88	95.0	.258	.421	12.61	1.4752	2.48
	B	3.35	4.38	3.56	.00	.019	3.54	80.8	.194	.388	12.28	1.4758	2.35
	C	3.44	3.96	3.10	.00	.011	2.95	74.5	.235	.383	13.54	1.4752	2.56
Highest		3.44	4.38	3.62	.00	.023	4.16	102.3	.424	.545	15.18	1.4760	2.56
Lowest		1.29	3.74	3.00	.00	.011	2.95	71.4	.194	.166	12.28	1.4750	2.00
Average		2.16	4.03	3.26	.00	.018	3.55	87.1	.285	.329	13.75	1.4754	2.27

[a] Archiv. Pharm., 1885, 827.

[b] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 13, Part 7, p. 908.

TABLE I.—*Analyses of roasted coffee and coffee substitutes.* (*Lythgoe*)—Continued.

Variety.	Cold-water extract	Alcohol extract	Reducing sugars.	Starch by diastase.	Crude fiber.	Caffeine.	Ten per cent extract.				
							Specific gravity at 15°.	Immersion refractometer reading at 20°.	Index of refraction at 20°.	Solids.	Ash.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*			n_D.	*Per ct.*	*Per ct.*
Santos A	20.80	16.83	0.52	2.28	13.41	1.25	1.0107	26.7	1.33770	2.64	0.40
Santos B	22.72	17.11	.68	1.00	11.02	1.10	1.0108	26.9	1.33777	2.66	.39
Santos C	21.70	17.80	.75	2.32	14.71	1.20	1.0101	26.0	1.33743	2.46	.30
Porto Rico A	22.48	15.70	.50	2.17	13.11	1.38	1.0107	26.6	1.33766	2.60	.37
Porto Rico B	21.76	16.36	.63	1.58	12.93	1.21	1.0104	26.3	1.33754	2.50	.36
Porto Rico C	24.44	16.91	.54	2.62	12.50	1.32	1.0113	27.6	1.33804	2.77	.30
Rio A	22.66	17.00	.68	2.82	14.08	1.11	1.0103	25.5	1.33724	2.48	.40
Rio B	22.61	17.34	.78	1.47	13.10	1.10	1.0101	25.8	1.33735	2.46	.36
Rio C	22.75	17.37	.61	2.62	11.91	1.17	1.0101	26.0	1.33743	2.46	.30
Mocha A	24.00	18.01	1.78	2.30	11.22	1.16	1.0106	26.4	1.33758	2.65	.40
Mocha B	20.27	17.96	.94	1.85	12.34	1.10	1.0101	26.3	1.33754	2.47	.36
Mocha C	24.18	19.55	1.42	2.90	13.20	1.18	1.0111	27.3	1.33793	2.72	.40
Java A	23.85	15.95	.32	2.95	13.43	1.34	1.0110	26.9	1.33777	2.63	.39
Java B	22.19	15.45	.42	2.32	13.77	1.30	1.0107	26.5	1.33762	2.58	.38
Java C	23.20	16.21	.66	3.34	14.75	1.27	1.0108	26.6	1.33766	2.62	.38
Highest	24.44	19.55	1.78	3.34	14.75	1.34	1.0113	27.6	1.33804	2.77	.40
Lowest	20.27	16.45	.32	1.00	11.02	1.00	1.0101	26.0	1.33743	2.46	.30
Average	22.63	17.03	.75	2.30	13.03	1.20	1.0105	26.6	1.33766	2.72	.37

[a] Omitted from average.

TABLE II.—*Analyses of coffee substitutes and of adulterated coffee.*

Variety.	Moisture.	Ash.	Water-soluble ash.	Sand.	Chlorin.	Alkalinity of—		Soluble P_2O_5.	Insoluble P_2O_5.	Petroleum-ether extract.	Index of refraction of extract at 30°.	Total nitrogen.
						Ash of 1 gram of substance	1 gram of ash.					
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*cc n/10 acid.*	*cc n/10 acid.*	*Per ct.*	*Per ct.*	*Per ct.*	n_D.	*Per ct.*
Roasted wheat	5.60	5.71	2.82	0.00	.....	0.34	6.0	0.649	1.460	2.40	.....	1.84
Roasted chicory	5.55	4.37	2.27	.81	0.080	.95	21.8	.277	.314	.88	.....	1.10
Coffee and chicory	5.08	3.96	3.14	.06	.026	3.05	77.0	.286	.323	8.32	.....	1.89
Coffee, chicory, and pea hulls	3.64	4.97	4.05	.24	[a].284	2.60	65.6	.472	.740	9.56	1.4745	2.17

[a] Admixture of salt.

TABLE II.—*Analyses of coffee substitutes and of adulterated coffee*—Continued.

Variety.	Cold-water extract.	Alcohol extract.	Reducing sugars.	Starch by diastase.	Crude fiber.	Caffeine.	Ten per cent extract.				
							Specific gravity at 15°.	Immersion refractometer reading at 20°.	Index of refraction at 20°.	Solids.	Ash.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*			n_D.	*Per ct.*	*Per ct.*
Roasted wheat.	25.88	10.72	4.10	28.58	6.23	0.00	.....	.....	.....	.....	.....
Roasted chicory	72.92	34.39	19.34	2.10	5.91	.00	1.0307	45.0	1.34463	7.44	0.26
Coffee and chicory.....	31.79	21.66	5.06	2.21	14.31	.95	1.0142	30.5	1.33915	3.62	.29
Coffee, chicory, and pea hulls	25.00	14.25	3.00	3.78	17.87	1.00	.....	.....	.....	.....	.....

The referee on food adulteration submitted the following report as associate referee on preservatives:

REPORT ON PRESERVATIVES.

By W. D. BIGELOW, *Associate Referee.*

The work on preservatives during the last year may be discussed under the following headings: (1) Methods for the detection of chemical preservatives in food; (2) a study of methods for the quantitative determination of preservatives; (3) the natural occurrence of chemical preservatives in fruit; (4) the influence of the process of canning on the content of chemical preservatives in food.

METHODS FOR THE DETECTION OF CHEMICAL PRESERVATIVES IN FOOD.

FORMALDEHYDE.

During the last few years several controversies have arisen with regard to the presence or absence of preservatives in food, giving increased interest to the study of the methods for the detection of such preservatives. In order to promote this work as far as possible a number of the methods that have been suggested during the last few years were abstracted by the referee and printed for distribution among those who had indicated their willingness to take part in the collaborative work of the year. Those receiving the circular were requested to try as many of the methods as possible and report their results to the referee. Although a large number of the members of the association had indicated their willingness to take part in the work, only three sent in results. I give below a summary of the work of Fred L. Flanders, of the Washington State College; J. J. Donald, district analyst, Montreal, Ontario; W. L. Dubois, of the Division of Foods, Bureau of Chemistry, and the referee.

Method No. 1.

(E. Riegler. Pharm. Centralh., 1900, *40:* 769.)

Formaldehyde and other aldehydes yield a rose-red color when treated with phenylhydrazin hydrochlorid and sodium hydroxid. Two cubic centimeters of milk, 2 cc of water, and 1 gram of phenylhydrazin hydrochlorid are placed in a test tube and shaken until the latter is dissolved, then 10 cc of a 10 per cent sodium hydroxid solution are added and the mixture shaken for ½ minute. Milk containing 2 drops of commercial formalin in 100 cc takes on a rose-red color in from 2 to 10 minutes.

Mr. Dubois obtains the best results by using 2 cc of the solution under examination, 2 cc of water, 0.10 gram of phenylhydrazin hydrochlorid, 6 cc of sodium hydroxid, and a 10 per cent solution. The referee prefers the same proportions, with the exception that slightly better results were obtained with 8 cc of the sodium hydroxid solution than with the lesser quantity.

In the hands of the four analysts the method was considered to give distinct reactions for formaldehyde when present in from 1 to 2,000 to 1 to 40,000 parts. Acetic aldehyde gives a reaction very similar to that of formaldehyde when present to the extent of 1 to 10,000 and interferes with the determination when present to the extent of 1 to 30,000. Benzaldehyde in dilutions of 1 to 10,000 also gives a faint pink color. On the whole, this method is not sufficiently sensitive for the detection of formaldehyde in foods, and the interference of other aldehydes is a strong objection.

Method No. 2.

(Manget and Marion. Compt. rend., 1902, *135:* 584; abs. Chem. Centrbl., 1902, pt. 2, p. 1276.)

To detect formaldehyde in milk the author treats the milk with a small amount of amidol (diamidophenol—1, 2, 4) or amidophenol. After a few minutes, milk containing formaldehyde takes on a canary-yellow color. Even in dilution of 1 part in 50,000 the reaction is distinct. For detecting formaldehyde in meat jellies a few crystals of amidol are added to bouillon and shaken; in the presence of formaldehyde a yellow color is formed, which becomes a dark yellow on the addition of ammonia. In the absence of formaldehyde the color first formed is bright reddish-brown which is converted into blue by the addition of ammonia.

Mr. Flanders in his report does not give the limit of reliability for this method, but in the column devoted to that purpose merely states that the reaction is faint. His comment on the method is that the results are uncertain. No other reports on this method were received.

Method No. 3.

(A. Gustave Luebert. J. Amer. Chem. Soc., 1901, *23:* 682.)

Five grams of milk are placed in a flask with 5 grams of coarsely powdered potassium sulphate; 10 cc of sulphuric acid are poured down the side of the flask. If formaldehyde be present the potassium sulphate becomes violet in a few minutes, and the color gradually disperses through the entire liquid. If absent a brown color forms which rapidly changes to black.

The method was found to be unsatisfactory by the three analysts who examined it, owing to the fact that even in the absence of formaldehyde a violet color, which is distinguished from the formaldehyde reaction with difficulty, is given by the reagents.

Method No. 4.

(Eduard Baier. Zts. Fleisch. Milchhyg., *11:* 70; abs. Chem. Centrbl., 1901, pt. 1, p. 595.)

The sample is finely macerated with an equal amount of water, the mixture filtered and the filtrate treated with a saturated solution of bromin in potassium bromid until all proteids and coloring matter are precipitated and the liquid contains an excess of bromin as indicated by the color. The mixture is then filtered and 2 cc of the filtrate mixed with 2 drops of an aqueous 1 per cent solution of resorcin and the product so obtained treated with an equal volume of concentrated sulphuric acid care being taken not to mix the two layers. At the point of union of the two liquids a white cloud appears which is heavy or light according to the relative amount of formaldehyde present. In the middle of the white zone is a carmin red color and below is a range of yellow liquid. In great dilution the turbidity is scarcely noticeable and the reaction takes place much more slowly. The reaction takes place in the

presence of formaldehyde with spoiled meat, meat preserved with sulphites, smoked meat, fresh meat, and with milk. In the examination of milk the greater part of the casein is first coagulated by means of rennet, the filtrate from which is handled as above. Even in the absence of formaldehyde a brown color is formed which obscures the carmin red color, but not the white cloud. One part of formaldehyde may be detected in 25,000 parts of the solution.

The results reported on this method are at great variance with each other. Mr. Donald considers the method rather long and tedious for commercial work and somewhat uncertain in its results. Mr. Flanders places its limit of reliability at 1 to 2,000. His comment is that it is a very good test for strong solutions. The results obtained in the Bureau of Chemistry by Mr. Dubois and the referee were fairly satisfactory, it being found possible to detect formaldehyde when present to the extent of from 1 to 50,000 to 1 to 60,000 parts. It was found essential, however, that the excess of bromin be made as slight as possible. A strong excess of bromin greatly interferes with the reaction and diminishes its sensibility. This method has the same objections as Method No. 9 in that acetic aldehyde, benzaldehdye, and distillates from saccharin matter interfere with the reaction. With paraldehyde Mr. Flanders obtained a yellow precipitate with a green band. It is of some value, however, as a class reagent in the examination of meats.

Method No. 5.

(C. Arnold and C. Mentzel. Zts. Nahr. Genussm., 1902, *5:* 353.)

A red color is given by formaldehyde with ferric salts, especially in alcoholic solutions. Mix 5 cc of an alcoholic solution of the substance with 0.03 gram of phenylhydrazin hydrochlorid and 4 drops of ferric chlorid solution; from 10 to 12 cc of concentrated sulphuric acid are then added, keeping the mixture cool. An intense red color is formed. A precipitate is formed which can be dissolved by the addition of either concentrated sulphuric acid, keeping the liquid cool, or by alcohol. With meats and fats the formaldehyde should first be extracted with alcohol and the filtrate tested. Milk is shaken with an equal volume of absolute alcohol and the filtrate employed. In pale beers the coloring matter may be seen without previous treatment, and in dark beers in the froth when the mixture is shaken. In very dark beers it is necessary to add the reagent as directed above and extract with ether, subsequently evaporating the ethereal extract to dryness and treating the residue with alcohol and concentrated sulphuric acid, when the color reappears.

Mr. Dubois called attention to the fact that the amount of sulphuric acid called for in this method is excessive. From 1 to 2 cc are sufficient. The method was tried with varying amounts of phenylhydrazin hydrochlorid, and the amount specified in the method as outlined seemed satisfactory. These points were afterwards confirmed by the referee. For many reasons this method is to be strongly recommended. Mr. Donald preferred it to all the other methods he tried. He was able to detect 1 part of formaldehyde in 150,000 of solution with certainty, and considers the results exceedingly sharp and brilliant. With large percentages he notes that the color change is instantaneous even with minute quantities of formaldehyde.

Mr. Flanders places the limit of reliability of this method at 1 to 20,000, and its limit of sensibility at 1 to 50,000. Although in his hands the method did not prove as delicate as in the hands of the other analysts, he considers it a good test. Mr. Dubois and the referee both found it to be very delicate. They were able to detect formaldehyde by this method when present to the extent of 1 part in 50,000. It has the great advantage of being characteristic, as acetic aldehyde and benzaldehyde do not interfere with it. Mr. Flanders obtained a deep reddish-brown color by the action of this reagent on paraldehyde.

Method No. 6.

(C. Arnold and C. Mentzel. Chem. Zg., 1902, *26:* 246. Abs. J. Chem. Soc. (Lond.), 1902 (2), *82:* 367; abs. Chem. Centrbl., 1902, pt. 1, p. 1077.)

The following tests may be applied directly to liquid foods or an aqueous or alcoholic extract of solid foods:

In 3 to 5 cc of the liquid (milk, for instance) is dissolved a lump of phenylhydrazin hydrochlorid the size of a pea, 2 to 4 drops (not more) of a 5 to 10 per cent solution of sodium nitroprussid are added, and finally 8 to 12 drops of 10 to 15 per cent sodium hydroxid. In the presence of even traces of formaldehyde, a fairly permanent blue or bluish-green color is produced. The test is rendered still more delicate by substituting potassium ferricyanid for the nitroprussid, but it can not then be recommended for milk or meat preparations containing blood-coloring matter; in case of an alcoholic solution, this must be well diluted with water to prevent precipitation of potassium ferricyanid.

Milk is examined directly. Meat is finely comminuted, extracted with 2 volumes of hot water, and the liquid pressed out and employed for the test. Fats (5 to 10 grams) are warmed above the melting point with 10 cc of from 80 to 95 per cent alcohol, thoroughly shaken, cooled, poured through a moistened filter, and the filtrate employed.

Mr. Donald found that with potassium ferricyanid milk containing even large quantities of formaldehyde gave no reaction by precipitating the casein with acetic acid; filtering and applying the test to the filtrate, he succeeded in detecting 1 part of formaldehyde in 25,000 of milk. No report was made by this analyst upon the use of the method with sodium nitroprussid.

Mr. Flanders considers the method using sodium nitroprussid to be reliable in dilutions of 1 to 10,000. Using ferricyanid instead of nitroprussid, he finds the method reliable in dilutions of 1 part in 100,000. He considers the reaction to be clear and distinct, and commented on the reagent as being very sensitive. Mr. Dubois obtained a clear characteristic green reaction with nitroprussid in solutions as strong as 1 part in 70,000. In more dilute solutions up to 1 part in 100,000 a color was given, but it was not satisfactory, as the green tint became less and less marked, and a yellow tinge tending toward greenish brown was formed. The referee was unable to detect the presence of formaldehyde by the ferricyanid method in all cases in solutions more dilute than 1 part in 60,000, although ordinarily it seemed to be satisfactory in solutions of 1 part in 70,000 to 1 part in 80,000. Whenever the reaction is a distinct green the method may be regarded as satisfactory.

Acetic aldehyde and benzaldehyde give a red to brown color according to the strength of the solution. For this reason a reaction given by one of these aldehydes is somewhat similar in color to that given by formaldehyde in solutions more dilute than 1 part in 60,000 or 70,000. The presence of acetic aldehyde and benzaldehyde together with formaldehyde may therefore give a yellowish or yellowish-green tinge, whereas if formaldehyde were present alone the color would be pure green. The reaction for formaldehyde might therefore be masked by the presence of other aldehydes. As far as our experience has gone, however, when the clear green color is obtained it may be taken as a characteristic test for formaldehyde. Mr. Flanders obtained a deep red color by the action of the reagent on solutions of paraldehyde.

Method No. 7.

(E. Rimini. Ann. di Farmacol., 1898, p. 97; abs. Chem. Centrbl., 1898, pt. 1, p. 1152; abs. J. Soc. Chem. Ind., 1898, *17:* 697.)

The author gives two extremely sensitive color reactions, which are characteristic for formaldehyde only, and are specially suitable for the detection of the latter in milk. (1) Fifteen cubic centimeters of a very dilute formaldehyde solution are treated with 1 cc of a dilute solution of phenylhydrazin hydrochlorid, then with a few drops of freshly prepared sodium nitroprussid solution, and finally with concen-

trated caustic soda solution. A blue color is formed, which, after a long time, changes to red. This reaction is capable of indicating formaldehyde in milk, even in a dilution of 1 in 30,000. (2) The second reaction is obtained in a similar manner, except that iron chlorid is used instead of sodium nitroprussid, followed by concentrated hydrochloric acid, instead of caustic soda. This gives a red color, which changes, after some time, to orange yellow.

(1) This method is essentially the same as No. 1 (Riegler), but Mr. Flanders found it to be more sensitive and more satisfactory than that method and less satisfactory and delicate than the second method by Rimini. Instead of the blue coloration Mr. Donald obtained a greenish brown in the presence of formaldehyde, while in the absence of that substance he obtained a bright orange yellow. Mr. Flanders obtained a deep blue reaction and considers the method reliable in solutions of 1 part in 50,000. He obtained much more satisfactory results with it than with method No. 1, which is somewhat similar in reaction. In the referee's hands the method is somewhat more sensitive, but is open to the same objections, on account of the interference of other aldehydes, as method No. 1. Mr. Flanders obtained a reddish color with the reagent on solutions of paraldehyde.

(2) Here, again, the reports of the various analysts were widely different in regard to the sensitiveness of the reaction. Mr. Donald reports the method as good and sharp. He was able to detect 1 part of formaldehyde in 70,000 parts of solution. On account of the fact that it does not give an instantaneous color change but requires a few minutes to develop he considers it inferior to No. 5. Mr. Flanders considers the method reliable in solutions of 1 part in 100,000 and was able to obtain a reaction in solution of 1 part to 500,000. He obtains with paraldehyde a red color turning quickly to brown. Mr. Dubois regarded the method as reliable in solutions of 1 part to 30,000 and the referee obtained characteristic reactions in solutions of 1 part to 50,000. Notwithstanding the varying results as to sensibility the method received no unfavorable comment and, like No. 5, has the advantage that it is not a group reaction and is not interfered with by acetic aldehyde or benzaldehyde.

Method No. 8.

(D. Vitali. Boll. Chem. Farmac., 1898, *37:* 321; abs. J. Soc. Chem. Ind., 1898, *17:* 955.)

If to a weak solution of formaldehyde an equal bulk of a 4 per cent solution of a phenylhydrazin salt be added, a white cloudiness occurs, gradually becoming yellow, and after some hours yellowish red. The turbidity occurs at once in a 1 per cent solution as formaldehyde, while in a solution containing 1 part in 100,000 it appears after two or three hours. The amorphous solid which settles out is soluble in alcohol, and can be obtained in rhombic tables by evaporating this solution. If the mixture of formaldehyde and phenylhydrazin solution be allowed to evaporate to dryness, and the washed residue taken up with alcohol, the yellow solution reduces a drop of gold chlorid and gives a greenish liquid, which is reddened by sodium hydroxid solution. If the mixture of formaldehyde and phenylhydrazin solution be mixed, immediately on the appearance of the turbidity, with sodium nitroprussid and sodium hydroxid, an intense blue color is struck. This reaction can be used to detect formaldehyde in the presence of acetaldehyde, if the latter be not present in too great quantity, as acetaldehyde gives no color under the circumstances.

This method was found to be unsatisfactory by all who tried it. Mr. Flanders obtained a distinct reaction in solutions of 1 part in 500. Mr. Dubois reports only a slight cloudiness with formaldehyde when present in the amount of from 1 to 20,000. A heavy precipitate was obtained by him only in a 0.5 per cent solution of formaldehyde. In neither case did the filtrate become yellowish red. The method is not to be recommended for the detection of formaldehyde in small quantities.

Method No. 9.

(Method (b), Bulletin 65, Bureau of Chemistry, p. 108.)

Mr. Flanders reports this method as reliable in solutions of 1 part to 10,000. He considers it a good test, but makes no statement regarding the influence of interfering bodies. A greenish-yellow color was obtained by the action of the solution on paraldehyde.

The referee regards the method as of considerable historical interest, as it was one of the first methods commonly used. It has led, however, to great errors, owing to the fact that numerous other bodies interfere with the reaction. It is a class reaction for aldehydes and is also given with other reducing substances, as stated by Mr. Dubois and previously noted by Traphagen, Burke, and others. An interfering color is obtained with the distillates from saccharin matters of various sorts. This method is not without its value as a class reaction, but can only be used as an indication. All results by it should be confirmed by other methods.

The following illustrations of reactions obtained by interfering substances and showing the unreliability of the method were reported by Mr. Dubois:

(1) Fifty grams of cane sugar were dissolved in 100 cc of water, made acid with phosphoric acid, and 50 cc distilled. The distillate when tested by the above method gave a yellowish-brown ring.

(2) Twenty-five grams of sugar dissolved in 100 cc of water was inverted by heating twenty-five minutes with 5 cc of hydrochloric acid. Fifty cc were then distilled. The distillate yielded a decided red ring with phenol and sulphuric acid which could not be distinguished from the ring given by formaldehyde. A decided red ring was also obtained by using a dilute solution of milk sugar without distilling.

With the other methods for formaldehyde sugar distillates give no confusing reactions.

Method No. 10.

(Method (c), Bulletin 65, Bureau of Chemistry, p. 108.)

Mr. Flanders regards this method as reliable for solutions of 1 part to 100,000, and obtained a slight reaction with solutions of 1 part to 1,000,000. With solutions of paraldehyde a brown ring was obtained. Mr. Dubois found the reaction certain and characteristic with milk containing formaldehyde to the amount of 1 part in 150,000. He obtained no reaction with acetaldehyde nor with benzaldehyde.

This method has been for several years among the provisional methods of the association, but for a long time it was regarded as of value only as a preliminary method. The more it is compared with other methods, however, the more we are led to the conclusion that it is among the surest and safest, as well as the most delicate, of the methods known for the detection of formaldehyde.

This method suggests the use of various modifications, such as the substitution of other oxidization agents for ferric chlorid and of sulphuric for hydrochloric acid. In the examination of distillates and other solutions containing formaldehyde the method is also used, a portion of milk equal to the volume of the solution employed being added and mixed in before the addition of the reagent. In the case of milk this method was found to be more delicate than any of the others employed. It is only half as sensitive, however, as with other solutions, owing to the fact that the formaldehyde is diluted with an equal volume of milk. Like methods Nos. 5, 6, and 7 (2), it has also the advantage of not being a class reaction, and is not interfered with by the presence of acetaldehyde and benzaldehyde.

Method No. 11.

(Method (d), Bulletin 65, Bureau of Chemistry, p. 108.)

This method was tried by two analysts and found to be unsatisfactory. The method is only applicable to fairly strong solutions. It is not nearly so sensitive as when caustic alkali is used in place of sodium acetate. In Mr. Flanders's hands the method gave no color with solutions of paraldehyde.

Method No. 12.

(Paragraph 6, Bulletin 65, Bureau of Chemistry, p. 36.)

This method gives satisfactory results when the commercial sulphuric acid employed contains a sufficient amount of ferric salts. Mr. Flanders reported the method reliable in solutions of 1 part to 50,000. He also obtained a reaction with the reagent on solutions of paraldehyde. In the referee's hands the method varies according to the sulphuric acid employed in making the test. Owing to the irregularity of commercial sulphuric acid the method can not be expected to give uniform results. It is better to use pure acid and introduce a known amount of ferric salts to insure obtaining a reagent of uniform character. When that is done the method is essentially the same as method No. 10.

Method No. 13.

(Mulliken, Identification of Pure Organic Compounds, vol. 1, p. 24.)

Mix 6 drops of a cold saturated solution of gallic acid with 2 cc of the aldehyde solution under examination. Allow the mixture to flow gently down the side of an inclined test tube; take from 3 to 5 drops of pure concentrated sulphuric acid, impart a gentle rotatory motion to the liquids in such a manner as not to cause the disappearance of the two layers. In the presence of formaldehyde a pure blue ring is formed. Great care should be taken in making this test that the aldehyde solution be not too concentrated. A more characteristic color is obtained with dilute solutions.

Mr. Flanders reports this method reliable in solutions of 1 part in 100,000, and considers it a very good test. If paraldehyde be present instead of formaldehyde, a reddish brown ring is obtained. This method should be studied further.

Method No. 14.

Schiff's reagent.—Dissolve 2 grams of rosanilin or its hydrochlorid or acetate in 10 cc of a freshly prepared solution of sodium dioxid. Allow the solution to stand for several hours, or until it becomes colorless, or at most a faint yellow. Dilute with water to 200 cc and place in a bottle with well-fitting stopper. Mix a small portion of the aldehyde solution with the reagent prepared as described above, agitate, and let stand two minutes. The presence of aldehyde is indicated by the formation of a color that varies from pink to red according to the amount of aldehyde present.

Mr. Flanders comments on the method as one of the most sensitive and easily applied tests known. He finds it reliable for solutions of 1 part of formaldehyde in 500,000, and obtains the same reaction with paraldehyde. In the referee's hands the method has proven altogether unreliable, because, while very sensitive, its reaction is not at all characteristic for formaldehyde. The method is somewhat troublesome, since, while the reagent keeps fairly well when tightly stoppered and in a cool, dark place, it loses its sensitiveness from time to time and requires to be resensitized. The red color which is given by formaldehyde is produced by all other aldehydes and also by many other substances, such as free alkalis and even alkali salts of organic acids. It is the opinion of the referee that if the method is used at all a positive reaction obtained by it should only be used as an indication that the substance under examination should be subjected to a more reliable test.

Summary of Results.

From the above considerations it is the opinion of the referee that preference should be given to the following methods for the detection of formaldehyde in foods, in the order given:

First.—Method No. 10, heating with hydrochloric acid (or sulphuric acid) in the presence of a small amount of ferric chlorid and fresh milk, as described in Bulletin 65 of the Bureau of Chemistry, page 108, method (c).

Second.—Method No. 5, Arnold and Mentzel.

Third.—Method No. 7 (2), Rimini.

Fourth.—Method No. 6, Arnold and Mentzel.

Further work on this subject, and especially the trial of these methods by a larger number of people, would be of great interest and value. It is hoped that during the coming year other members of the association will have time and opportunity to take part in this work, in order that the methods which give the best results in the hands of the largest number may be selected. With the exception of those above noted it does not appear that any of the methods outlined by the referee need be given further study by the association, unless it be method No. 13, using gallic and sulphuric acids. It would be well during the coming year for a study to be made of the old phloroglucin method to determine its value in comparison with those outlined above. It must also be borne in mind that many of the reactions for the detection of formaldehyde are class reactions, and great care must be taken not to misinterpret the indications. It is the opinion of the referee that in the detection of formaldehyde reactions obtained by any one method, except by hydrochloric acid or sulphuric acid and ferric chlorid for the detection of formaldehyde in milk, should always be confirmed by other methods before coming to a decision regarding the presence of that substance.

The Detection of Formaldehyde in Milk.

It has long been known that on standing the amount of formaldehyde in milk decreases, and if only a small amount be added it will speedily disappear. It is doubtless true, therefore, that many samples of milk taken for analysis and reported to be free from formaldehyde have really had formaldehyde added to them in small amount, but owing to its tendency to disappear or go into combination with other substances it can no longer be detected. If this substance actually disappeared from the milk altogether and left no objectionable compound the question would not be so serious. Considering the fact, however, that formaldehyde is known to go into combination with the proteids of milk and that the resulting compound is believed to be relatively indigestible, it becomes important to know not only whether formaldehyde is present in the milk at the time it is served to the consumer, but whether it has ever been added. It also is necessary for us to know what method will give positive results at the longest time after the addition of a small amount of formaldehyde to milk.

To determine this point, milk was preserved with amounts of formaldehyde varying from 1 part in 5,000 to 1 part in 10,000 of milk and tested by several methods until the formaldehyde entirely disappeared. The results of this work are given in Table I. The methods employed were No. 10, hydrochloric acid and ferric chlorid; No. 9, phenol and sulphuric acid; No. 1, phenylhydrazin and sodium hydroxid; No. 5, alcohol and ferric hydroxid; No. 6, phenylhydrazin and potassium ferricyanid; and No. 7, using phenylhydrazin, hydrochlorid, ferric chlorid, and hydrochloric acid.

The milk without previous treatment was subjected to examination by all of these methods. During a portion of the time also the milk was distilled and the distillates examined by all methods except method No. 10, which is not applicable. It appears that in the sample in which 1 part of formaldehyde was added to 50,000 parts of milk the formaldehyde disappeared entirely after twenty-four hours, so that no reaction could be obtained by any of the methods given. For the treatment of the original milk method No. 10 (hydrochloric acid and ferric chlorid) is incomparably better than the other methods employed. By distillation, however, formaldehyde is not only separated from the fat, casein, and coloring matter, and so brought into such condition that much more delicate results can be obtained by the other methods, but it is also materially concentrated, by far the greater portion of the formaldehyde passing over with the first part of the distillate. Notwithstanding, therefore, the marked superiority of method No. 10 over the other methods applied for the examination of milk, methods Nos. 1, 5, 6, and 7 are apparently equally delicate if the milk be previously distilled.

TABLE I.—*Formaldehyde in milk.*

Concentration.	Age of preserved sample.	Reactions with milk.						Reactions with distillate.				
		Method No. 10. Hydrochloric acid and ferric chlorid.	Method No. 9. Phenol and sulphuric acid.	Method No. 1. Phenyl hydrazin and sodium hydroxid.	Method No. 5. Alcohol and ferric hydroxid.	Method No. 6. Phenyl hydrazin and potassium ferricyanid.	Method No. 7. Phenyl hydrazin, ferric chlorid, and hydrochloric acid.	Method No. 9.	Method No. 1.	Method No. 5.	Method No. 6.	Method No. 7.
	Days.											
1–10,000	1	Good	Good	Good	.....	.....	Good	.....	.....	.....	Good	Good.
1–10,000	2	Good	Good	Good	Good	Good	Good	.....	.....	.....	Good	Good.
1–10,000	3	Good	Good	Good	Good	Good	Fair	.....	.....	.....	Good	Good.
1–10,000	4	Good	.....	Fair	Faint	Fair	Faint	.....	.....	.....	Good	Good.
1–10,000	5	Good	None	None	None	None	None	Faint	Faint	Good	Fair	Good.
1–10,000	6	Good	None	None	None	None	None	Faint	Faint	Good	Fair	Fair.
1–10,000	7	Fair	None	None	None	None	None	Faint	None	Faint	Faint	Faint.
1–10,000	8	Fair	None	None	None	None	None	Very faint.	Very faint.	Fair	Fair	Faint.
1–10,000	10	Faint	None	None	None	None	None	None	Very faint.	Fair	[a]Faint	Very faint.
1–10,000	12	Very faint.	None	None	None	None	None	None	None	Faint	[a]Faint	None.
1–10,000	13	Very faint.	None	None	None	None	None	None	None	Very faint.	None	None.
1–10,000	16	Very faint.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
1–25,000	1	Good	Good	Fair	Fair	Fair	Fair	.....	.....	.....	Good	Good.
1–25,000	2	Fair	Fair	Faint	Faint	Faint	Faint	.....	.....	.....	Fair	Good.
1–25,000	3	Fair	Faint	Faint	Faint	Faint	None	.....	.....	.....	Fair	Fair.
1–25,000	4	Faint	None	None	None	None	None	.....	.....	.....	Faint	Faint.
1–25,000	5	Very faint.	None	None	None	None	None	None	None	None	None	None.
1–25,000	6	None	None	None	None	None	None	None	None	None	None	None.
1–50,000	1	None	None	None	.....	.....	None	.....	.....	.....	None	None.
1–50,000	2	None	None	None	None	None	None	.....	.....	.....	None	None.

[a] Color greenish brown; not characteristic.

SACCHARIN.

Method No. 1.

(Methods of Blarez and Carlos modified by Chace.)

Rep. pharm. (3) *6*: 110, 111. La revue commerciale et coloniale, December 12, 1903.

Fifty cubic centimeters of wine are acidified and extracted with ether. The extracted matter is tested in the usual way for salicylic acid, the gasoline extract being returned to the dish containing the residue, the whole diluted to about 10 cc volume, and 2 cc one-third sulphuric acid added. The solution is brought to the boiling point, and concentrated potassium permanganate added drop by drop to slight excess, the solution partly cooled, a piece of sodium hydroxid added, and filtered into a silver dish (crucible lids are used in this laboratory), evaporated to dryness and heated for twenty minutes at 210° to 215° C. The residues are dissolved in water, acidified and extracted with ether, the ether evaporated and residues tested with two drops of a 0.5 per cent solution of ferric alum.

By this method all the so-called false saccharin and the salicylic acid up to 10 milligrams per liter are destroyed, while one-half milligram of saccharin per liter is detected with absolute certainty and one-eighth milligram per liter is detected in the majority of tests.

This method was confirmed by Mr. Dubois, who considers it well adapted to the purpose for which it is intended. Further work by Mr. Chace confirmed his previous experience with this method, which it is hoped will be studied by other members of the association during the coming year, as it may frequently be of great value.

Method No. 2.

(A. Leys. Ann. chim. anal., 1901, *6*: 201; abs. Analyst, 1901, *26*: 321.)

If 10 cc of a very dilute solution of copper sulphate or of a ferric salt be mixed with two or three drops of hydrogen peroxid, and warmed with an aqueous solution of an unsaturated organic compound, an intense brown coloration is produced. This reaction is obtained with salicylic acid, benzoic acid, cinnamic acid, saccharin, acetanilid, ortho-phenylene-diamine, antipyrine, pyrrhol, thiophen, and furfurol. No color is obtained with alcohol, acetic acid, lactic acid, sucrose, allyl acetate, fumaric acid, menthol, or turpentine.

The brown coloration given by saccharin can be prevented by the addition of a trace of sulphuric acid, and even after warming the mixture for a few moments only a faint yellow tint is produced. After a short time two drops of a very dilute solution of ferric chlorid are added, and a violet coloration is obtained. This reaction, which is due to formation of oxybenzoic acid, is also given by benzoic acid. By using very dilute solutions of ferric chlorid and hydrogen peroxid in the cold the addition of the acid is rendered unnecessary.

Saccharin in milk.—Fifty cc are treated with 100 cc of a 10 per cent solution of potassium bisulphate, to each 100 cc of which has been added 10 cc of 99 per cent alcohol, and the precipitated casein filtered off. The filtrate is shaken with two portions of ether, crystals of bisulphate that may separate during the second extraction are redissolved with a few drops of alcohol, the ethereal extracts are evaporated to dryness at 90° C, and the residue dissolved in 5 cc of boiling water. When cold the solution is tasted, and, if sweet, is tested with two drops of a very dilute solution of ferric chlorid and 2 cc of dilute hydrogen peroxid and left for thirty minutes. In the presence of saccharin a violet tint is slowly developed.

Saccharin in butter.—Dissolve the butter in a mixture of equal volumes of chloroform and absolute alcohol; add twice the volume of water, shake, allow to settle, and separate. The separated chloroform retains the fats; the aqueous-alcoholic solution contains the saccharin. Evaporate the latter and test as above.

The ferric chlorid solution is prepared by diluting 2 cc of a solution of 30° Bé. to 100 cc, and the hydrogen peroxid by diluting 1 cc of the ordinary 10 volume (3 per cent) solution to 200 cc.

Mr. Dubois was the only one reporting on this method. No color whatever was obtained when operating with copper sulphate. Warming a dilute solution of ferric chlorid alone a brown coloration was obtained which could not be distinguished from

that given in the presence of saccharin. He regards the method as entirely impracticable.

Method No. 3.

(Matteo Spica. Gazz chim. ital., 1901, pt. 2, *31*: 41; abs. J. Chem. Soc. (Lond.), 1901, pt. 2, *80*: 704.)

The author has devised two methods for the detection of small proportions of saccharin in commercial products. The first of these consists in converting the imino group of the saccharin into nitric acid, which is recognized by means of diphenylamine hydrochlorid, whilst in the second method the saccharin is transformed into one of the sulphaminobenzoic acids, which can be detected by the diazo-reaction. The method of working is as follows: The liquid to be tested, acidified with sulphuric acid, or, in the case of a solid, the extract obtained with the dilute acid is shaken in a separating funnel with ether or a mixture of ether and light petroleum, the liquid being then filtered and divided amongst three dry test-tubes, which are placed in a water bath to evaporate. The residue in one tube is tested for salicylic acid by adding nitric acid and heating gently to form picric acid, which is recognized by the method previously described.[a] To the second residue is added a little lime, best somewhat granular as obtained from powdered marble, and the mixture then heated until it becomes slightly brown; a few cubic centimeters of water are then added, the liquid heated to boiling, and the clear solution decanted off into another tube, where it is mixed with a few drops of hydrochloric acid and a small piece of zinc; after hydrogen has been evolved for twenty minutes the liquid is again decanted off and to it are added a few drops of dilute sodium or potassium nitrite solution and 5 to 6 drops of a naphthylamine hydrochlorid solution; in the event of "saccharin" being present in the substance examined, a crimson coloration is obtained which only appears after some hours if the quantity of "saccharin" is very small. To the residue in the third tube are added a few drops of pure sulphuric acid and a crystal of potassium permanganate, oxidation being started by gentle heating, and the excess of permanganate removed by means of oxalic acid or sulphur dioxid. The liquid is then diluted with a few cubic centimeters of water, a few drops of diphenylamine hydrochlorid are added, and pure sulphuric acid poured carefully down the side of the test-tube so as to form a distinct layer at the bottom. The presence of nitric acid, produced from "saccharin," is manifested by an azure-blue ring in the layer between the sulphuric acid and the aqueous liquid.

The time spent upon this method was not sufficient to give any decisive results. Apparently, if the method is reliable, considerable experience with it is necessary, as the results obtained were unsatisfactory.

Method No. 4.

(E. Riegler. Pharm. Centralh., 1900, *41*: 563; abs. Chem. Centrbl., 1900, pt. 2, p. 880.)

If from 0.01 to 0.02 gram of saccharin be dissolved in 10 cc of water and be treated with 2 drops of 10 per cent sodium hydroxid solution, and *p*-diazonitroanilin be added, drop by drop, with constant shaking, a greenish yellow liquid will first form and then disappear. The liquid is then shaken with 10 cc of ether, and from 20 to 30 drops of 10 per cent solution of sodium hydroxid added. At the point of contact between the ether and sodium a fine green ring is formed, and on shaking the ether turns green and the alkali a yellowish brown. If the aqueous layer be removed and 5 cc of concentrated ammonia are added to the ethereal portion, the latter is decolorized while the ammoniacal portion turns a distinct green.

Salicylic acid treated in the same manner gives an intense red ring and a red aqueous solution, but the supernatant ether is colorless. On treatment of ethereal layer with ammonia the ether remains colorless, but the ammoniacal liquid turns red. If saccharin and salicylic acid are both present a red, though somewhat brown, ring is first obtained, the ether is turned green and the aqueous solution red. On the addition of ammonia the ether becomes colorless and the aqueous liquid violet. The color of the aqueous layer varies in shade according to the relative amounts of salicylic acid in saccharin present. The reagent is prepared by dissolving 2.5 grams of *p*-nitranilin in 25 cc of water and 5 cc of strong sulphuric acid. When the solution becomes clear, 25 cc of water are added and 1.5 grams of sodium nitrite dissolved

[a] Abs. J. Chem. Soc. (Lond.), 1895, pt. 2, *68*: p. 426.

in 20 cc of water are also added and the whole diluted to 250 cc. This solution may be kept for a long time in the dark without being decomposed. If it becomes turbid it may be filtered, and the filtrate may still be employed.

The results obtained by Mr. Dubois and the referee with this method were unsatisfactory. Mr. Dubois found the method to be sensitive to 0.5 milligram of salicylic acid, but impracticable for detecting either benzoic acid or saccharin. He obtained the same results with a solution of 0.5 milligram of salicylic acid, a solution of a mixture of 0.5 milligram of salicylic acid and saccharin, and a solution of a mixture of 0.5 milligram each of salicylic acid and benzoic acid.

Method No. 5.

(Official Russian Method. Zeit. Ver. Zucker-Ind, 1901, *38:* 95.)

The following is the official Russian method as adopted by the customs authorities for the detection of saccharin in food:

Solid and sirupy substances are first diluted with two parts of water, filtered, and the filtrate tested. In the case of beer and other substances containing hops a saturated solution of copper nitrate is added until no further precipitate is formed. In all cases where tannin is present a small amount of ferric chlorid solution is added and the liquid made slightly alkaline with calcium carbonate and filtered for the purpose of removing tannin. The following methods are recommended for the detection of saccharin:

1. One hundred cubic centimeters of the liquid are acidified with hydrochloric acid, treated with an excess of bromin water, well shaken and filtered. The filtrate (or supernatant liquid removed by decantation) is treated with a current of air to remove the bromin, extracted with ether, and the presence of saccharin detected in the ether extracted by the taste and by the presence of salicylic acid after fusing with caustic potash.

2. One hundred cubic centimeters of the liquid are made strongly acid with hydrochloric acid and shaken with equal parts of ether and petroleum ether. The residue from the volatile solvent is converted into salicylic acid by fusing for one-half hour in a glycerin bath at 250° with caustic soda.

Salicylic acid, if present, is removed as the bromin compound by the first method.

a. *Tests of saccharin.*—The ether extract is evaporated and the residue is warmed with resorcinol and concentrated sulphuric acid and the mixture poured into an excess of caustic soda solution. The presence of saccharin is indicated by a strong fluorescence, which is interfered with by succinic acid when present.

b. *Second method.*—The substance is treated with concentrated nitric acid, the solution evaporated to dryness and a few drops of a solution of caustic potash in 50 per cent alcohol added. On rewarming, a blue color, changing to violet, then to purple red, and finally to red, is formed in the presence of saccharin.

No results were obtained regarding these methods with the exception of those of Mr. Dubois, which are as follows:

1. Bromin is found to remove salicylic acid completely from solutions containing both salicylic acid and saccharin. The method was tried and found to be satisfactory on amounts of saccharin as small as 5 milligrams. This method was made the basis of other work on the separation of preservatives, which is given below.

2. This method is one which is very familiar to all chemists who have worked at all with saccharin. It is found by Mr. Dubois to be satisfactory with as small a quantity as 5 milligrams, and was not tried with less than that amount.

(a) This method was found to be unsatisfactory with a smaller quantity of saccharin than 50 milligrams.

(b) No report.

Method No. 6.

(H. Defournel. J. pharm. chim., 1901, *13:* 512; abs. Chem. Centrbl., 1901, pt. 2, p. 60.)

The liquid is acidified with sulphuric acid and extracted with ether, as usual, or with a mixture of equal parts of ether and petroleum ether. The volatile solvent is separated, washed with water to remove acids, and evaporated to dryness. The residue is treated with ammonia, the excess of which is expelled by evaporation on

the water bath. It is then dissolved in a small amount of water and transferred to an ordinary urometer, in which it is decomposed by means of hypobromite. The volume of nitrogen expressed as tenths of a cubic centimeter, divided by 8.9, gives the weight of saccharin in centigrams.

No results were reported regarding this method. It is included as a part of the report with the hope that it may be tested during the coming year.

Detection of Salicylic Acid, Benzoic Acid, and Saccharin in the Presence of Each Other.

It is generally recognized that methods for the quantitative determination of chemical preservatives are very desirable, and that in some cases they may be necessary. Considerable attention was given to the problem of separating salicylic acid, benzoic acid, and saccharin, and the difficulties connected with the determination of salicylic acid in such mixtures were fairly well solved. The work is still unfinished, however, with regard to benzoic acid and saccharin. The methods employed by Mr. Dubois for the determination of salicylic acid are given below.

A Study of Methods for the Quantitative Determination of Chemical Preservatives.

salicylic acid.

Method No. 1.

Salicylic acid was precipitated by means of bromin water, using sufficient excess of the latter to impart a decided bromin color to the solution. This precipitate was filtered, dried, and weighed. It was found that precipitation is complete and that even minute traces of salicylic acid may be removed from solutions by means of bromin water. The precipitate formed, however, is of a sticky character, and, although it filters very nicely, retains bromin with a great deal of tenacity. No satisfactory method was found for completely removing the bromin from the precipitate. It was also found that by heating this precipitate at the temperature of boiling water much of it was apparently lost. The difficulties experienced in handling the precipitate were such that the method was given up for what seemed to be a better one.

Method No. 2.

This method is essentially that given in Sutton's Volumetric Analysis, latest edition. The method depends upon the formation of a definite body when salicylic acid is brought into contact with bromin. This body, when treated with potassium iodid, undergoes a change, in which potassium is substituted for bromin. The latter reaction takes place in a definite way. The bromin necessary for the reaction is obtained from a standard solution of potassium bromate and potassium bromid, the bromin being set free by hydrochloric acid. From 75 to 100 per cent excess of bromin is necessary. The solutions required are a standard solution of sodium thiosulphate, conveniently decinormal, and a standard solution of potassium bromate and potassium bromid, containing approximately 2.5 grams potassium bromate and about 10 grams of potassium bromid in a liter of water. The thiosulphate solution is standardized as usual by means of potassium dichromate and potassium iodid. The strength of the bromate solution, using the quantities of bromate and bromid given above, is approximately decinormal.

The required quantity of bromid and bromate solution is diluted with 300 cc of water and decomposed with 30 cc of hydrochloric acid (sp. gr. 1.1). Into this is introduced an approximately 1 per cent solution of the substance under examination, stirring constantly during addition. A white precipitate is formed immediately, and after allowing this to stand 5 minutes with occasional agitation, from 30 to 40 cc of a

10 per cent solution of potassium iodid are introduced, and the separated iodin titrated with thiosulphate. Too great an excess of bromin or too long standing of the precipitate will cause a loss in iodin titration. In cases of substances containing starch or sugar, water must not be used as a solvent for the material for the same reason. Instead of water 90 per cent alcohol is used.

When applying this method to wines the sample is made alkalin, concentrated, acidified with sulphuric acid, and extracted repeatedly with ether. The ether solution is evaporated, the residue taken up with alkalin water, and this solution run by the method given above. The best results were obtained by using a thiosulphate solution of such strength that 1 cc was equivalent to 0.01028 gram of iodin and to 0.001864 gram of salicylic acid. One cc of the bromin solution was equivalent to 1.092 cc of thiosulphate.

The results obtained with method No. 2 by Mr. Dubois are given below in tabular form and are, on the whole, encouraging. It is probable that the low figures obtained with raspberries are due to incomplete extraction. Unfortunately there was not time to try the quantitative determination of salicylic acid in the presence of benzoic acid and saccharin.

TABLE II.—*Estimation of salicylic acid.*

AQUEOUS SOLUTION.

Amount added.	Amount found.	Amount added.	Amount found.
Gram.	*Gram.*	*Gram.*	*Gram.*
0.0500	0.0544	0.0025	0.0029
.0500	.0544	.0030	.0033
.0050	.0056	.0040	.0043
.0100	.0107	.0050	.0052
.0005	.0005	.0100	.0110
.0010	.0011	.0200	.0229
.0015	.0017	.0300	.0358
.0020	.0021	.0400	.0458

RASPBERRIES.

0.1250	0.0379	0.0125	0.0077
.1250	0652	.0125	.0094

WINE.

[a] 0.0200	0.0207	0.0200	0.0246
[a] .0350	.0304	.0250	.0275
[a] .0500	.0399	.0300	.0354
[b] .0300	.0283	.0400	.0428
[b] .0200	.0237	.0500	.0495
[b] .0100	.0097	.....	.....

[a] Extracted 3 times with ether. [b] Extracted 4 times with ether.

BENZOIC ACID.

A reliable method for the determination of benzoic acid has long been desired. There have been no methods suggested by means of which even approximately accurate results could be obtained. In connection with the study of the occurrence of benzoic acid in the cranberry a quantitative method became necessary and four methods which suggested themselves were compared with a view to using them in that study.

Method No. 1.

An attempt was made to extract the benzoic acid by means of ether, evaporate the ether, and dissolve the residue in a sufficient quantity of dilute sodium hydroxid to make it exactly neutral. An effort was then made to determine the temperature at which the benzoic acid present, liberated by means of sulphuric acid, would dissolve and recrystallize from the warmer solution, when, by means of a table the volume of liquid being known, the amount of benzoic acid present could be estimated.

When working with solutions of benzoic acid in water fairly reliable results could be obtained. Great difficulty was found, however, with extracts from vegetable substances. It became necessary to purify the benzoic acid in the ether extract by redissolving in gasoline, and when it was purified other more reliable methods presented themselves for its determination.

Method No. 2.

This method was suggested by Mr. A. L. Winton. Considerable difficulty was found in devising an apparatus which would answer all requirements, but finally the efforts made in this direction were successful. The apparatus used is shown in fig. 1.

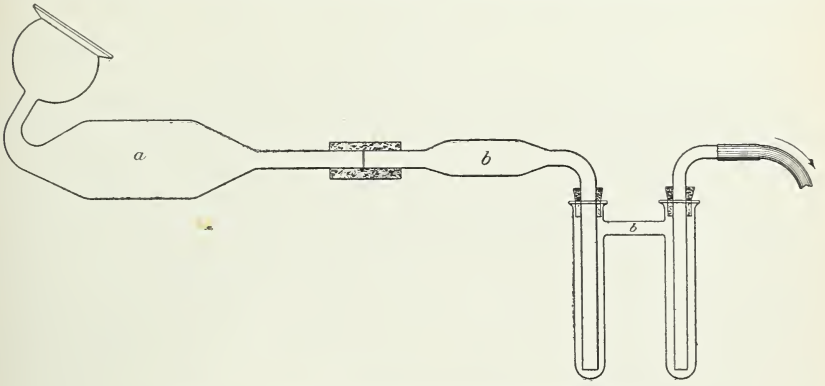

FIG. 1.—Apparatus for the determination of benzoic acid.

The method depends on the fact that benzoic acid boils at about 145° C. The aqueous solution of the substance under examination—in the case of cranberries the aqueous extract of the berries—is repeatedly extracted with ether, the ether concentrated by evaporation and transferred to a bulb tube (a) which may be conveniently constructed from a 50 cc pipette and a small glass funnel. The remainder of the ether is then evaporated from the tube by passing a slow current of air through it, and the tube is kept in a sulphuric acid desiccator until thoroughly dry. It is then connected by means of a cork stopper with the weighing tube (b) in such a way that the tube (a) is on the inside of a bath or oven that may be heated gradually until the temperature of 250° C is reached.

At the beginning of the operation the apparatus should be pushed to the left so that the bulb of the tube (b) is in the edge of the oven. After the benzoic acid has begun to sublime the tube may be moved to the right to such a distance that the acid will sublime into the bulb of the tube (b). Care must be taken in this respect that the acid shall not be condensed in the narrow part of the tube (b), and it must be closed before the operation is complete. Considerable difficulty was experienced in securing a tube that would condense the sulphuric acid completely. The one employed here, which was suggested by R. M. Bird, gave very satisfactory results.

It was necessary to exercise great care in the heating, as when a temperature slightly too high was reached the organic matter decomposed and a black tarry mass passed over into the tube (b). The apparatus was employed, however, with quite a number of organic substances, and usually that difficulty could be avoided, though in some cases it was necessary to extract the benzoic acid from the residue with chloroform or gasoline.

Method No. 3.

Owing to the fact that in the two preceding methods it was sometimes necessary to purify the benzoic acid obtained in the ether extract by means of gasoline it seemed probable that sufficiently accurate results could be obtained by weighing directly the benzoic acid so separated. Accordingly the aqueous extract of the fruit was extracted repeatedly with ether, the ether allowed to evaporate to dryness in a beaker, placed in a sulphuric acid desiccator until thoroughly dry, and the residue extracted repeatedly with low boiling point gasoline. The gasoline solution of benzoic acid was evaporated to dryness in a tared beaker, the gasoline evaporated, and the amount of benzoic acid determined by weighing. This method was found to give equally as good results on the fruits examined as methods Nos. 1 and 2. In foods containing a considerable amount of fat, however, or other substances soluble in gasoline, method No. 2 is to be preferred to method No. 3.

Method No. 4.

It was found that very satisfactory results could be reached by titrating the benzoic acid obtained by methods Nos. 2 and 3. This procedure was used in confirming all of the results obtained by those methods, and the results were usually sufficiently close for all practical purposes. Care of course must be taken to exclude all sulphuric acid which may be introduced in extracting with ether the acidified aqueous extract. The benzoic acid residue after the evaporation of the gasoline solution, as described under methods Nos. 2 and 3, is evaporated to dryness, a few drops of alkali solution of phenolphthalein added, and the residue titrated directly with standard alkali solution. A small amount of water may be introduced before the titration, but if the amount of residue is considerable the addition of water is unnecessary, as the volume of standard alkali employed will afford sufficient liquid to dissolve the sodium hydroxid formed.

The Natural Occurrence of Preserving Chemicals in Fruits.

The normal occurrence of boric acid in grapes, and hence in wine, has been known for a number of years, and attention is called to it in Part 3 of Bulletin 13 of the Bureau of Chemistry. In 1890 also the occurrence in wine of a substance having all the reactions for salicylic acid was reported by Medicus.[a]

In 1900 considerable attention was drawn to the presence of salicylic acid in wine by an error that was made in the examination of wine in which 150 cc had been used as a sample. It was pointed out that Medicus in 1890 had called attention to the possibility of this error and to the fact that not more than 50 cc should be used in the detection of salicylic acid in wine, owing to the natural occurrence of a small amount of a *body giving the same reaction*. This error, however, led to the examination of a number of natural fruits. In Table III are given the results of various analysts on a wide range of fruits. It is thus seen that salicylic acid occurs in fruit quite frequently. At the same time it is evident that the amount present is not sufficient to lead to analytical error, considering the amount of substance ordinarily taken for examination.

[a] Ber. 9te Verein. bayr. Vertr. ang. Chem., 1890, s. 42.

TABLE III.—*Salicylic acid occurring naturally in fruit.* (*Compiled.*)

Substance.	Amount in 1 kilogram of fruit.	Analyst.
	Mg.	
Apples	None	Süss.
Do	Amount not determined	Traphagen and Burke.
Apricots	None	Windisch.
Do	Amount not determined	Traphagen and Burke.
Bilberries	None	Utz.
Blackberries	do	Süss.
Do	Amount not determined	Traphagen and Burke.
Cherries	0.40	Do.
Do	None	Süss.
Cherries, wild	20.0–30.0	Jablin-Gonnet.
Cherries	None	Windisch.
Do	0.10–0.21	Desmoulieres.
Crabapples	0.24	Traphagen and Burke.
Cranberries	None	Süss.
Do	0.15–0.35[a]	Bigelow.
Currants	0.57	Traphagen and Burke.
Currants, red	None	Süss.
Do	do	Utz.
Currants, red, white, and black	do	Windisch.
Gooseberries	do	Süss.
Do	do	Utz.
Gooseberries, red and white	do	Windisch.
Grapes	0.32	Traphagen and Burke.
Green gages	None	Süss.
Do	do	Windisch.
Mahonia berries	do	Do.
Peaches	do	Do.
Do	Amount not determined	Traphagen and Burke.
Pears	None	Süss.
Plums	do	Do.
Do	do	Windisch.
Do	0.28	Traphagen and Burke.
Raspberries	None	Süss.
Do	Amount not given	Utz.
Do	1.1[b]	Windisch.
Do	Amount not determined	Traphagen and Burke.
Strawberries	2.0–3.0	Süss.
Do	Amount not given	Utz.
Do	2.8[b]	Windisch.
Do	1.0	Portes and Desmoulieres.
Do	Reaction[c]	Mastbaum.
Do	Amount not determined	Traphagen and Burke.
Wine[d]	0.0–0.825	Mastbaum.
Do	0.9	(?)

[a] See page 62.

[b] In the juice.

[c] The salicylic acid was not determined quantitatively. It was present in sufficient quantity to give a reaction in the juice from 100 grams of fruit.

[d] Red and white wines of various origin.

Benzoic acid has also been reported in several fruits. During the early summer Mr. Glenn F. Mason called the attention of the referee to the fact that cranberries contained a much larger amount of benzoic acid than was usually supposed. He also forwarded a residue from the ether extract of 300 grams of cranberries, which the referee found contained 80 milligrams of benzoic acid—that is, benzoic acid was pres-

ent in the ratio of 260.66 milligrams per kilogram. These cranberries Mr. Mason said had been bought in the Allegheny, Pa., market in the month of May. A sample of cranberries bought at the same time by Mr. Mason was also found by the referee to contain a similar amount of benzoic acid. This sample, however, was in a very bad state of preservation. The berries were soft and considerable juice had exuded. Mr. Mason suggested the importance of giving this matter further study.

Through Mr. William A. Taylor, pomologist in charge of field investigations of the U. S. Department of Agriculture, arrangements were made with the following men to secure samples of cranberries at intervals during their growth and ripening: A. D. Makepeace, Wareham, Mass.; E. H. Durell, Belleplain, N. J., and L. P. Haskins, Grand Rapids, Wis. During the early stages of the growth of the cranberry a small reaction with ferric chlorid, resembling that of salicylic acid, was obtained equivalent to the reaction of from 0.15 to 0.35 milligram of salicylic acid per kilogram of fruit. The residue obtained by extracting the berries with volatile solvents was not sufficiently purified to yield a clear characteristic reaction with ferric chlorid. Only about 110 grams were available for extraction, and the color of the ferric compound was very light. The presence of salicylic acid, therefore, was not confirmed, but a substance was evidently present during the early part of the season which gave a purple or purplish-brown color with ferric chlorid. The samples received after August 5 gave no reaction for salicylic acid nor any reaction similar to it, but did contain benzoic acid. Those received on August 5 and 6 contained but a trace of benzoic acid, and the amount gradually increased until the berries began to redden. After that time it increased rapidly till the berries were fully ripe. The berries then contained from 210 to 430 milligrams of benzoic acid per kilogram. Samples of ripe berries have been placed in cold storage to determine if any change results in the benzoic acid content.

In the latter part of August, 1904, two samples of cranberries, grown in 1903 and preserved in cold storage, were obtained in the Horticultural Building at the St. Louis Exposition. One of these samples was grown in Wisconsin and the other in Virginia. The two samples contained, respectively, 230 and 220 milligrams of benzoic acid per kilogram.

The Influence of the Process of Canning on the Content of Chemical Preservatives in Food.

During the last ten years there has been a number of disputes between food laboratories and manufacturers of food products with regard to the presence of chemical preservatives in canned goods. Manufacturers whose goods were alleged to contain food preservatives sometimes offered the strongest assertions that none had been added. Some of these cases were explained by the fact that there had been used preservatives sold under trade names with the assurance that they contained none of the ordinary chemical preservatives, and could be used in full compliance with all food laws. Sometimes these compounds were even sold for other alleged purposes than preservation, and manufacturers have frequently asked whether it was not possible that these preservative chemicals occurred naturally in the fruits and vegetables and were formed in the operations to which the foods are subjected in the process of canning. During the last four years considerable attention has been paid to the natural occurrence of these preservative substances in fresh fruits.

It has been pointed out above that although preserving chemicals do exist to a small extent naturally in many fruits, still, with the possible exception of benzoic acid in cranberries and one or two other berries of the same class, these substances are not found in nature to a sufficient amount to lead to error in analytical work. The question as to whether these preserving chemicals might be formed by the operations to which the food is subjected in the process of canning remained to be answered.

Considering the enormous number of canned fruits and vegetables that have been examined in the various food laboratories of this country during recent years the relatively small percentage reported as containing any commercial preservative is almost conclusive proof that such preservatives are not formed by the heat of processing. If they were so formed their presence would be universal. However, practical canners have for many years suggested this theory as a possible explanation of some laboratory reports which they could not otherwise account for, and one of them announced that he had proved that such was the case. Considering the fact that there is no account in any scientific publication of the formation of any of these substances in the way mentioned, and that such a reaction is unknown, their formation under such conditions would seem to be entirely improbable. At the same time it seemed possible that some other substances might be formed which might give a similar reaction to that given by the preservatives, or in some way mask or interfere with the reaction. It seemed advisable, therefore, to undertake this study, and it was begun with the collaboration of Mr. Dubois. Samples of raspberries, blackberries, string and wax beans, sweet corn, beef, tomatoes, and navy beans (for the preparation of baked beans) were secured and canned according to the process ordinarily used for those substances, except that the temperature used was somewhat higher than is frequently used with some of the articles enumerated. In all something over 200 cans of various articles were processed, some without the addition of any preserving chemical whatever, others containing varying definite amounts of salicylic acid, benzoic acid, formaldehyde, and saccharin, respectively. The cans were all heated in boiling water for from 10 to 12 minutes to expel air before closing the vent. After the vent was closed they were processed under steam pressure at a temperature of 250° F. (121.1° C). The raspberries and blackberries were divided in two lots, one of which was heated 12 minutes and the other 40 minutes.

The corn, string beans, and wax beans were processed for 55 minutes at a temperature of 250° F (121.1° C). The baked beans were soaked over night in water, after which they were canned, as indicated above, and processed for 1 hour at a temperature of 250° F (121.1° C). The meat was cut up into pieces of uniform size, parboiled for 30 minutes, sealed, as indicated above, and processed for 2 hours at 250° F (121.1° C). As a still more critical test 1 dozen cans of the meat were processed for 2 hours at a temperature of 167° C. The tomatoes were cooked until soft, after which they were canned, as indicated above, and processed for 1 hour at 250° F (121.1° C).

Each of these substances was canned, as follows: Without the addition of any preservative whatever; with the addition of formaldehyde in quantities varying from 1 part in 5,000 to 1 part in 25,000; and with the addition of benzoic acid, salicylic acid, and saccharin in quantities varying from 0.5 to 0.05 gram per kilogram. In the tins canned without any preservative each of these preservatives was tested for by several methods, with negative results. Indistinct and uncertain colors were sometimes obtained with some methods. In some cases these colors bore a certain remote resemblance to those given by the tests for the preservative chemical in question, and might possibly have confused one unfamiliar with the reaction who had not prepared himself by careful experiments with known substances. No reaction was obtained, however, which should under any circumstances confuse or mislead a chemist who had made a careful study of methods for the detection of food preservatives and who is qualified for that work.

Since it appeared that no substances were formed with a reaction similar to those of any chemical preservatives, the next step was to determine whether the preservatives actually present in canned goods were destroyed or changed in such a way as to prevent or lessen the reaction by which they are detected, or to interfere in any way with their detection. The work on this subject has not been completed, and the food canned with known amounts of preservatives for the most part is held for further work. In a few instances the amount of salicylic acid and benzoic acid has been

determined, and the results obtained were identical with the amount added, considering the usual limit of error for these determinations.

With formaldehyde the case is quite different. It was found that when the amount of formaldehyde added to the food before canning was not greater than 1 part in 7,000 not the slightest reaction for formaldehyde could be obtained in any case with the canned product processed at 250° F (121.1° C). When formaldehyde was added in greater amounts than 1 part in 7,000 a reaction was obtained in every instance, faint in the more dilute solutions, but marked when the concentration was greater. The formaldehyde was determined quantitatively in all cans, and while the amount which had resisted the processing was not uniform it seemed to bear no relation to the time of processing. Cans processed for 20 minutes contained no more formaldehyde than those processed for from 50 minutes to 1 hour. In every case, however, it was evident that by far the greater part of the formaldehyde had been destroyed, decomposed, combined with some other substance, or at any rate so changed that it does not respond to any known reaction for formaldehyde. Food to which had been added 1 part of formaldehyde in 5,000 before canning, after canning contained but 1 part in 100,000.

During recent years formaldehyde has several times been reported in canned goods. The articles canned with the larger quantities of formaldehyde were relatively tough and uninviting. According to the results just given it would appear that if present in canned goods it must have been added to the food before canning to an extent greater than 1 part in 7,000. The necessity of adding formaldehyde in such quantities for the preservation of food is not obvious. The practice of using it in such quantities in milk or in other articles of food is unknown. If formaldehyde is used in the canning industry to such an extent that a reaction in the canned article can still be obtained, the matter should be carefully studied. If, on the other hand, our analytical methods are misinterpreted or lead to incorrect results, further study on that subject is essential. In any case, considering the contrary results that have been obtained with various analytical methods, no reaction for formaldehyde in any other food than milk should ever be reported as the result of using a single method, and an unusual amount of experience and judgment is essential to the proper manipulation of these tests and the interpretation of their results.

Recommendations.

It is recommended—

1. That method (b), page 108 of Bulletin No. 65, for the determination of formaldehyde, be discontinued.

2. That methods 5, 6, and 7 (2), for determining formaldehyde, be given further trial by the association, as well as the following method, on which no work was done this year:

(D. M. Jorissen. Service de Surveillance des Aliments en Belgique; through Bull. soc. chim. Paris, 1897, p. 167. Abs. Analyst 1897, *22*: 282.)

Several drops of a 10 per cent aqueous solution of phloroglucinol are added to about 10 cc of the milk, the mixture shaken, and a few drops of a solution of caustic soda or potash added. A red coloration is produced with milk containing as little as 1 part of formalin in 20,000, while normal milk gives no reaction.

The referee on beer then presented the following report:

REPORT ON BEER.

By H. E. Barnard, *Associate Referee.*

In presenting a report of the work that has been accomplished in the past two years on beer there is but little to offer in the way of analytical investigations. In the analysis of beers the methods employed are, for the most part, not peculiar to beer alone, and with but little alteration are well adapted to their purpose. Never-

theless there are several changes to be suggested in the methods as published in Bulletin 65 of the Bureau of Chemistry, which will produce more satisfactory results than those provisionally adopted.

Since the brewer is more deeply interested in any analytical study of beers and has given more time to the subject than the chemist who works on beers simply as a part of his studies, I have consulted the men at the head of the brewing institutes as well as the members who so kindly offered to cooperate in the work. To both I am indebted in great measure for whatever suggestions I have to offer in regard to beer analysis.

Taking up the various sections under beer, as given in the Provisional Methods for the Analyses of Foods,[a] the following changes and modifications, with the reasons which make their adoption advisable, are given:

B. Beer.

1. *Preparation of sample.*—As given, care being taken that the beer is not below 15° C, since below that temperature carbon dioxid is retained in the beer and is liable to form bubbles in the pycnometer.

2. *Determination of specific gravity.*—As given. Attention is called to the fact that the chemists who are engaged in brewing and brewery work make their determinations at 15° C, and that their tables, ballings, etc., are calculated at that temperature. As a matter of fact we are already using 15° C tables—the tables by Schultz and Ostermann, and those by Ellion on extract in beer wort being so calculated. For the sake of uniformity our tables should be recalculated to the same standard for all work.

3. *Determination of alcohol.*—Measure 100 cc of beer, free from carbon dioxid, into an Erlenmeyer flask of from 300 to 500 cc capacity; add 50 cc of water; attach the flask to a vertical condenser by means of a bent tube and distill up to the mark of a 100 cc graduated flask. Foaming may be prevented by placing a piece of asbestos board under the flask. Cool to 15.6° C, and bring to the mark; determine the specific gravity of the distillate as directed under 2, and obtain the corresponding percentage of alcohol, by volume and grams per 100 cc, from Table II, p. 121, Bulletin 65.

4. *Determination of extract.*—Ascertain the extract content corresponding to the specific gravity of the dealcoholized beer according to Table III, p. 127, Bulletin 65. For this purpose employ the formula $sp = g + (1 - a)$, in which *sp* is the specific gravity of the dealcoholized beer, *g* the specific gravity of the beer, and *a* the specific gravity of the distillate obtained in the determination of alcohol.

5. For "Determination of original gravity of wort" read "Determination of the percentage of extract and specific gravity of original wort." This change is advisable because of the importance of knowing the "Extract of wort," or "Balling of wort," i. e., the number of pounds of extract contained in 100 pounds of wort. Use the method as given, referring to Table III to determine the percentage of extract, noting, however, the statement by the brewing institutes that this method does not give satisfactory results. In calculating the percentage of extract in original wort use is made of the formula $O = 2A + E$, in which *O* is the original extract of the wort, *E* the extract of the dealcoholized beer, and *A* the alcohol of the beer. The specific gravity is then found by referring to the table. In this formula it is considered that sugars yield one-half their weight of alcohol when fermented. Verification of this formula and comparison with the authorized formula is not possible in the ordinary laboratory, but the fact that the latter formula is used by the brewers of this country makes its reliability worth considering.

6. *Determination of the degree of fermentation.*—Calculate from the formula $D = \frac{200a}{B}$, in which *D* is the degree of fermentation, *a* the percentage of alcohol, and *B* the percentage of extract originally contained in the wort from which the beer was pro-

[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 65, p. 92.

duced. The formula given in Bulletin 65 does not express the degree of fermentation, which means the number of parts of extract fermented in 100 parts of original extract. The formula suggested gives in per cent the amount of original extract fermented, a most satisfactory and lucid way of representing just what has taken place. The formula $D = \frac{100sp}{G}$ gives a factor which might be employed for purposes of comparison, but which is entirely lacking in clearness of definition.

7. *Determination of total acids.*—As given.

8. *Determination of volatile acids.*—The volatile acid, as acetic acid, is determined by titrating 20 cc of the alcoholic distillate with decinormal sodium hydroxid solution, using phenolphthalein as an indicator. The number of cubic centimeters of decinormal alkali employed multiplied by 0.030 gives the acidity expressed as grams of acetic acid per 100 cc.

9. *Determination of reducing sugars.*—Twenty-five cc of beer free from carbon dioxid is diluted with water to 100 cc. The reducing sugar is determined in 25 cc of this solution, as directed on page 49, the solution being boiled 4 minutes instead of 2. Express the results in terms of maltose equivalent to copper reduced, according to Table IX, page 144, Bulletin 65.

10. *Determination of dextrin.*—Employ Sachsse's method for the hydrolization of starch and determine dextrose according to Allihn, as follows:

Fifty cc of beer and 15 cc of hydrochloric acid, specific gravity 1.125, are diluted to 200 cc, attached to a reflux condenser and kept in a boiling water bath for 2 hours. Neutralize with caustic soda and dilute to 250 cc (or 300 cc in a beer with high extract). Add 25 cc of the diluted solution to the boiling Fehling solution and boil 2 minutes. Multiply the oxid of copper found by 0.8 to obtain the corresponding amount of copper and refer to Allihn's dextrose table (Table VIII, page 143, Bulletin 65). The amount of dextrose thus found multiplied by 20 (or 24 if diluted to 300 cc) and divided by the specific gravity equals the dextrose in the original beer. From this figure subtract 95 per cent of the amount of maltose in the original beer and multiply the remainder by 0.9, the result being the percentage of dextrin in the original beer.

11. *Determination of glycerol.*—Proceed as directed on page 82. The milk of lime is added during evaporation after the carbon dioxid has been expelled. It is advisable that the filtrate after being evaporated to a sirupy consistency be treated again with 5 cc of absolute alcohol and 2 portions of 7.5 cc each of absolute ether. If clear, continue as directed. If not clear, it is necessary to treat again as before.

12. *Determination of ash.*—As given.

13. *Determination of phosphoric acid.*—Measure out 50 cc of the original beer, free from carbonic acid, into a small beaker. Add 5 cc of an acid solution of sodium acetate and heat to boiling. Run in, from a burette standard, uranium acetate solution, one-half cc at a time, testing each time until a drop of the beer, when placed on a white plate, colors a drop of potassium ferrocyanid slightly brown. The number of cubic centimeters of the uranium acetate solution necessary, multiplied by 0.01, gives the per cent of phosphoric acid in the beer. If the beer is very dark employ the official gravimetric or volumetric method, using the residue obtained in the determination of the ash.

14. *Determination of protein.*—Evaporate 25 cc of the original beer, to which has been added a small amount of tannin to prevent frothing, and proceed according to the Kjeldahl or Gunning method for the determination of nitrogen and multiply the result by 6.25.

15. *Determination of carbon dioxid.*—As given.

16. *Detection of preservatives.*—As given.

One other suggestion occurs to me which is in accordance with the recommendation of President Davidson, in his address last year, to change the temperature at

which our apparatus is graduated from 15.5° C to a temperature more nearly in accordance with room temperature, and that is that our alcoholometric tables be revised so that we shall not have to make pycnometer weighings at a temperature five or ten degrees below room temperature. Because it has been the custom in European laboratories to work at a temperature of about 15° C, we have adopted tables calculated on a basis of that temperature and have been put to endless trouble thereby. It may be that the change would be so revolutionary as to be inadvisable. Yet, as I have shown, there seems to be no good reason for working along on such an arbitrary temperature standard if a change can be made.

One other problem in connection with the analysis of beer has been given considerable attention. That is the working out of some practical and accurate method for identifying the so-called glucose and malt substitute beers. To secure as much advice as possible from men who have had had some experience in beer work there was sent to each of the chemists who had expressed their desire to collaborate in the work, and also to the directors of several of the brewing academies and institutes, a circular letter suggesting the need of a method and calling attention to the usual custom of relying on the amount of phosphoric acid, sulphates, and nitrogenous matter for identifying the beer. The replies received showed that there is no uniformity of practice on the subject, but that each chemist has set for himself some standard by which to judge the composition of a beer.

C. L. Parsons[a] gives the average analysis of 76 beers which he concludes were brewed from malt, and the detailed analyses of five beers which he considered to be non-malt. He bases his conclusions on the amounts of phosphoric acid, albuminoids, and sulphates found in the beers. While it is true that some of the so-called temperance beers which are produced with the aid of but little malt may have a very low phosphoric acid and albuminoid content, the content of phosphoric acid and nitrogen in pure malt beers varies to such an extraordinary extent that in the opinion of the referee the amount of these ingredients can not be taken as evidence of the employment of either glucose, corn, or rice.

In support of this statement the analyses of a number of American and imported beers from tables in the Wahl-Heinus American Handy-Book of Brewing and Malting are given below:

TABLE I.—*Analyses of imported and American beers (Wahl-Heinus).*

Name of brand.	Original extract.	Albumen.	Phosphoric acid.	Lactic acid.
Imported:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
No. 1	15.03	0.47	0.0675	0.099
2	15.30	.44	.08	.24
3	13.85	.44	.05	.09
4	[b]14.55	.46	.08	.108
5	[b]17.13	1.12	.105	.18
6	[b]15.03	1.08	.088	.148
7	[b]15.69	.51	.095	.135
American:				
Stock ale, average of nine samples	[b]16.74	.46	.061	.256
Sparkling ale	[b]14.20	.38	.04	.135
Porter	[b]13.25	.40	.061	.166
Weissbeer	[b]9.50	.42	.036	.342
Beer brewed from Montana barley malt	14.34	.66	.09	.108
Beer brewed from Minnesota barley malt	14.18	1.13	.12	.108

[a] Am. Chem. Soc., 1902, *24*: p. 1174.

[b] Calculated.

It is evident from a comparison of these analyses that there is a wide variation in the albuminoid and phosphoric acid contents of beers of the same original extract content. For instance, the albumen content of the beer brewed from Minnesota barley malt is almost twice as high as in the case of beer brewed from Montana barley malt, while the phosphoric acid content is also much higher. It is evident that in using a barley malt like that from Minnesota from 40 to 45 per cent of glucose could be employed before the albumen content would fall below the content normal to the Montana barley malt. Or the brewer could employ 25 per cent of rice of grits with the Minnesota barley malt without being open to the charge, on account of too low phosphoric acid content, of having employed anything but pure malt. The imported beer No. 6, for instance, has 1.08 per cent of albumen, while the imported beer No. 1, with exactly the same percentage of original extract, contains but 0.47 per cent of albumen—less than one-half the albumen content of No. 6. The imported beer No. 3 contains an amount of phosphoric acid equivalent to 3.6 per cent of the original extract, while No. 7 contains nearly double that quantity, or 6 per cent of the original extract—that is to say, in the brewing of No. 7 approximately 50 per cent of unmalted cereals or glucose might have been employed and still an amount of phosphoric acid be found in the beer equivalent to beer No. 3. In some of these pure malt beers we find a low percentage of albumen and a high percentage of phosphoric acid, like No. 7; in another we find a high percentage of albumen and a high percentage of phosphoric acid, like No. 5. If, then, the brewer uses the proper malts, having both high percentages of albumen and phosphoric acid, he can employ cereals and glucose without the possibility of detection. The sulphuric acid content of beer does not depend, as has been supposed by some chemists, upon the use of impure glucose, but upon the character of the brewing water. It is, moreover, a common practice to treat waters with sulphate of lime, or "Burtonizing" it, to increase the hardness.

It is evident that if we are to find any method of differentiating between all malt beers and beers brewed in part from substitutes work must be undertaken along entirely different lines from those followed up to the present time.

A résumé of the report on fats and oils was given by Mr. Weber in the absence of the referee. This report is as follows, the complete details of the work being published as Circular No. 22 of the Bureau of Chemistry.

REPORT ON FATS AND OILS.

By L. M. Tolman, *Associate Referee.*

The Titer Test.

The titer test has been the subject of study in the association for two years. The various modifications of the test in use in this country did not give concordant results, and several of the largest business houses using it expressed a desire that this association should cooperate with them, a similar arrangement having been made in the case of the tannin methods, in the preparation of a satisfactory and uniform method. As a preliminary step samples of fat were sent to nineteen chemists to determine what methods were in use and how the results obtained by the different modifications would agree. The instructions for this work and its results are given in full in the proceedings of the association for 1903.[a]

It was found that modifications of two methods were in general use in this country, but that the details of the methods, as carried out in the different laboratories, were varied and could only lead to diversity of results. It was evident that a uniform method and a uniform thermometer were essential, and two typical methods were selected for further work, i. e., the Dalican method as used by James Boyce, of the American Cotton Oil Company, and the Wolfbauer method as used by A. G. Manns, of Armour & Co. These methods are also given in full in the proceedings.[b]

The work on these methods in 1904 was conducted on four samples of fat—oleo stearin, edible tallow, yellow grease, and cotton-seed oil—sent to the various chemists desiring to cooperate, together with a circular on the methods,[c] requesting that the titer of the fatty acids prepared by the different methods of saponification be taken by both methods of stirring and that the thermometer readings for the stem exposure be corrected by the following formula:

$$T = T' + u(T' - t)\ 0.000154.$$

T=observed temperature.

u=length of mercury column above the fat in degree divisions of the thermometer.

t=room temperature.

The reports of 25 chemists on the four samples of fat are collected in Tables I and II.

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[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 81, p. 65.

[b] Ibid., p. 66, 71.

[c] Circular issued by the Bureau of Chemistry, February 24, 1904, on proposed work on the titer test by the Association of Official Agricultural Chemists.

COOPERATIVE WORK.

TABLE I.—*Results of cooperative work on the titer test for 1904—Wolfbauer method of stirring.*

Analyst.	1 Oleo stearin.				2 Edible tallow.			
	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
F. C. Weber, U. S. Department of Agriculture	50.55	24	50.6	23	42.2	25	42.35	23
A. H. Schmidt, Schwarzschild & Sulzberger, Chicago	50.60	24	50.6	16	42.3	24	42.40	16
L. M. Tolman, U. S. Department of Agriculture	50.70	23	50.67	18	42.3	23	42.30	23
David Wesson, Southern Cotton Oil Company, New York	50.88	25	50.94	26	42.46	27	42.43	26
A. G. Manns, Armour & Co., Chicago	50.91	.....	.....	.....	42.55	.....	.....	.....
W. E. Tinney, Armour & Co., South Omaha, Nebr	50.40	25	50.3	25	42.45	27	42.45	25
Garland Jones, Armour & Co., Fort Worth, Tex	50.5	37	.....	.....	42.50	31	.....	.....
C. F. Hagedorn, Armour & Co., National Stock Yards, Ill	50.4	28	50.26	28	41.71	28	42.19	28
A. V. H. Mory, Armour Packing Company, Kansas City	50.4	25	50.80	26	42.41	26	42.83	26
James Boyce, American Cotton Oil Company, Chicago (1)	50.4	.....	.....	.....	41.80	.....	.....	.....
James Boyce, American Cotton Oil Company, Chicago (2)	50.83	.....	.....	.....	42.62	.....	.....	.....
James Boyce, American Cotton Oil Company, Chicago (3)	50.78	.....	.....	.....	42.44	.....	.....	.....
James Boyce, American Cotton Oil Company, Chicago (4)	50.82	.....	.....	.....	42.41	.....	.....	.....
R. D. Oilar, Wilcox Lard Company, New York	50.55	27	.....	.....	42.10	30.7	.....	.....
J. E. Weber, Procter & Gamble, Cincinnati, Ohio	.....	.....	.....	.....	42.10	24	42.2	20
M. H. Ittner, Colgate & Co., New York	50.65	.....	50.30	.....	42.25	.....	41.85	.....
Wilson Low, Cudahy Packing Company, Kansas City, Mo	.....	.....	50.57	22	.....	.....	42.30	23
W. D. Richardson, Swift & Co., Chicago	.....	.....	.....	.....	.....	.....	.....	.....
E. K. Nelson, Nelson Morris & Co., Chicago	50.5	.....	.....	.....	42.5	.....	.....	.....
A. H. Gill, Massachusetts Institute of Technology, Boston	50.6	30	.....	.....	42.2	30	.....	.....
A. G. Stillwell, Stillwell Provisioner Laboratory, New York	50.35	23	.....	.....	41.85	23	.....	.....
Stillwell & Gladding, New York	.....	.....	[a]50.0	.....	.....	.....	[a]42.2	.....
Larkin Soap Company, Buffalo, C. W. C	50.85	.....	.....	.....	42.30	.....	.....	.....
Larkin Soap Company, Buffalo, W. W. S	50.85	.....	.....	.....	42.00	.....	.....	.....
Larkin Soap Company, Buffalo, J. C. T	50.85	.....	.....	.....	.....	.....	.....	.....
Average	50.64	.....	50.50	.....	42.26	.....	42.32	.....
Maximum	50.91	.....	50.94	.....	42.62	.....	42.83	.....
Minimum	50.35	.....	50.26	.....	41.71	.....	41.85	.....
Difference	.56	.....	.68	.....	.91	.....	.98	.....

[a] Not corrected for stem exposure.

TABLE I.—*Results of cooperative work on the titer test for 1904—Wolfbauer method of stirring*—Continued.

Analyst.	3 Yellow grease.				4 Cotton-seed oil.			
	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
F. C. Weber, U. S. Department of Agriculture	40.58	25	40.7	25	35.4	25	35.85	25
A. H. Schmidt, Schwarzschild & Sulzberger, Chicago	40.30	24	40.2	16	34.8	24	34.40	16
L. M. Tolman, U. S. Department of Agriculture	40.68	25	40.5	24	35.3	22	34.90	22
David Wesson, Southern Cotton Oil Company, New York	40.58	26	40.45	26	34.9	25	34.87	26
A. G. Manns, Armour & Co., Chicago	41.13	.....	.....	.....	35.29	.....	.....	.....
W. E. Tinney, Armour & Co., South Omaha, Nebr	41.00	27	40.8	25	.....	.....	34.6	27
Garland Jones, Armour & Co., Fort Worth, Tex	41.00	31	.....	.....	34.4	32	.....	.....
C. F. Hagedorn, Armour & Co., National Stock Yards, Ill	40.33	28	40.28	28	35.26	28	35	28
A. V. H. Mory, Armour Packing Company, Kansas City	41.00	28	40.90	25	[a]32.90	27	36.75	26
James Boyce, American-Cotton Oil Company, Chicago (1)	40.90	.....	.....	.....	33.9	.....	.....	.....
James Boyce, American Cotton Oil Company, Chicago (2)	40.40	.....	.....	.....	34.45	.....	.....	.....
James Boyce, American Cotton Oil Company, Chicago (3)	40.37	.....	.....	.....	34.17	.....	.....	.....
James Boyce, American Cotton Oil Company, Chicago (4)	40.55	.....	.....	.....	34.89	.....	.....	.....
R. D. Oilar, Wilcox Lard Company, New York	40.59	28	.....	.....	34.74	29	.....	.....
J. E. Weber, Procter & Gamble, Cincinnati, Ohio	40.70	24	40.7	20	35.50	21	35.6	21
M. H. Ittner, Colgate & Co., New York	40.20	.....	39.68	.....	35.0	.....	34.9	.....
Wilson Low, Cudahy Packing Company, Kansas City, Mo	.....	.....	40.89	23	.....	.....	35.25	23
W. D. Richardson, Swift & Co., Chicago	.....	.....	.....	.....	.....	.....	.....	.....
E. K. Nelson Nelson Morris & Co., Chicago	40.80	.....	.....	.....	35.3	.....	.....	.....
A. H. Gill, Massachusetts Institute of Technology, Boston	40.60	30	.....	.....	35.1	30	.....	.....
A. G. Stillwell, Stillwell Provisioner Laboratory, New York	40.30	22	.....	.....	34.7	22	.....	.....
Stillwell & Gladding, New York	.....	.....	[b]40.35	.....	.....	.....	[b]34.4	.....
Larkin Soap Company, Buffalo, C. W. C	40.72	.....	.....	.....	.....	.....	.....	.....
Larkin Soap Company, Buffalo, W. W. S	40.22	.....	.....	.....	34.09	.....	.....	.....
Larkin Soap Company, Buffalo, J. C. T	.....	.....	.....	.....	33.90	.....	.....	.....
Average	40.62	.....	40.50	.....	34.7	.....	35.14	.....
Maximum	41.13	.....	40.90	.....	35.5	.....	36.85	.....
Minimum	40.20	.....	39.68	.....	32.9	.....	34.40	.....
Difference	.93	.....	1.22	.....	2.6	.....	2.45	.....

[a] Scorched.

[b] Not corrected for stem exposure.

TABLE II.—*Results of cooperative work on the titer test for 1904—Dalican method of stirring.*

Analyst.	1 Oleo stearin.				2 Edible tallow.			
	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
F. C. Weber, U. S. Department of Agriculture	50.11	23	50.08	24	41.58	25	41.55	25
A. H. Schmidt, Schwarzschild & Sulzberger, Chicago	50.10	24	49.90	16	41.80	24	41.90	16
L. M. Tolman, U. S. Department of Agriculture	50.20	23	50.00	22	41.68	22	41.68	26
David Wesson, Southern Cotton Oil Company, New York	50.39	25	50.40	25	41.91	26	41.86	27
A. G. Manns, Armour & Co., Chicago	.....	.....	.....	.....	.....	.....	41.26	.....
W. E. Tinney, Armour & Co., South Omaha, Nebr	50.00	26	49.90	24	41.60	26	41.35	25
Garland Jones, Armour & Co., Fort Worth, Tex	.....	.....	50.00	34	.....	.....	41.90	35
C. F. Hagedorn, Armour & Co., National Stock Yards, Ill	49.97	28	49.73	28	41.58	28	41.59	28
A. V. H. Mory, Armour Packing Company, Kansas City	50.10	25	49.73	22	41.70	25	41.80	22
James Boyce, American Cotton Oil Company, Chicago (1)	.....	.....	50.20	.....	.....	.....	41.70	.....
James Boyce, American Cotton Oil Company, Chicago (2)	.....	.....	50.30	.....	.....	.....	41.63	.....
James Boyce, American Cotton Oil Company, Chicago (3)	.....	.....	50.23	.....	.....	.....	41.79	.....
James Boyce, American Cotton Oil Company, Chicago (4)	.....	.....	50.38	.....	.....	.....	41.82	.....
R. D. Oilar, Wilcox Lard Company, New York	50.02	31	50.02	31	41.95	31	41.82	30
J. E. Weber, Procter & Gamble, Cincinnati	.....	.....	.....	.....	41.40	23	41.50	20
M. H. Ittner, Colgate & Co., New York	50.45	.....	50.12	.....	42.23	.....	41.87	.....
Wilson Low, Cudahy Packing Company, Kansas City, Mo	.....	.....	50.25	23	.....	.....	41.57	23
W. D. Richardson, Swift & Co., Chicago	.....	.....	50.00	22	.....	.....	42.00	22
E. K. Nelson, Nelson Morris & Co., Chicago	.....	.....	49.85	.....	.....	.....	41.65	.....
A. H. Gill, Massachusetts Institute of Technology, Boston	.....	.....	49.70	30	.....	.....	41.70	30
A. G. Stillwell, Stillwell Provisioner Laboratory, New York	.....	.....	50.05	20	.....	.....	41.75	20
Stillwell & Gladding, New York	.....	.....	49.95	.....	.....	.....	42.10	.....
Larkin Soap Company, Buffalo, C. W. C	.....	.....	50.32	.....	.....	.....	.....	.....
Larkin Soap Company, Buffalo, W. W. S	.....	.....	50.20	.....	.....	.....	.....	.....
Larkin Soap Company, Buffalo, J. C. T	.....	.....	50.15	.....	.....	.....	.....	.....
Average	50.15	.....	50.06	.....	41.74	.....	41.72	.....
Maximum	50.45	.....	50.40	.....	42.23	.....	42.10	.....
Minimum	49.97	.....	49.70	.....	41.40	.....	41.26	.....
Difference	.48	.....	.70	.....	.83	.....	.84	.....

TABLE II.—*Results of cooperative work on the titer test for 1904—Dalican method of stirring*—Continued.

Analyst.	3 Yellow grease.				4 Cotton-seed oil.			
	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.	Wolfbauer fatty acids.	Room temperature.	Dalican fatty acids.	Room temperature.
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
F. C. Weber, U. S. Department of Agriculture	39.78	25	39.30	25	33.93	25	33.75	24
A. H. Schmidt, Schwarzschild & Sulzberger, Chicago	39.40	24	39.70	16	33.80	34	33.60	16
L. M. Tolman, U. S. Department of Agriculture	39.90	25	39.50	22	34.05	25	33.85	21
David Wesson, Southern Cotton Oil Company, New York	39.60	27	39.57	27	33.35	26	33.31	26
A. G. Manns, Armour & Co., Chicago	.....	.....	38.72	.....	.....	.....	33.05	.....
W. E. Tinney, Armour & Co., South Omaha, Nebr	39.50	26	39.30	25	.....	.....	32.30	27
Garland Jones, Armour & Co., Fort Worth, Tex	.....	.....	40.10	35	.....	.....	33.50	25
C. F. Hagedorn, Armour & Co., National Stock Yards, Ill	39.62	28	39.17	28	33.74	28	33.92	28
A. V. H. Mory, Armour Packing Company, Kansas City	39.40	25	39.50	24	31.75	25	33.55	25
James Boyce, American Cotton Oil Company, Chicago (1)	.....	.....	39.50	.....	.....	.....	33.60	.....
James Boyce, American Cotton Oil Company, Chicago (2)	.....	.....	39.30	.....	.....	.....	33.60	.....
James Boyce, American Cotton Oil Company, Chicago (3)	.....	.....	39.83	.....	.....	.....	33.26	.....
James Boyce, American Cotton Oil Company, Chicago (4)	.....	.....	39.98	.....	.....	.....	33.83	.....
R. D. Oilar, Wilcox Lard Company, New York	39.69	29	39.43	28	33.16	31	34.05	31
J. E. Weber, Procter & Gamble, Cincinnati	39.60	21	39.50	21	33.10	19	33.10	21
M. H. Ittner, Colgate & Co., New York	40.15	.....	40.16	.....	34.03	.....	34.26	.....
Wilson Low, Cudahy Packing Company, Kansas City, Mo	.....	.....	39.85	23	.....	.....	33.05	23
W. D. Richardson, Swift & Co., Chicago	.....	.....	40.20	22	.....	.....	34.10	22
E. K. Nelson, Nelson Morris & Co., Chicago	.....	.....	39.75	.....	.....	.....	33.55	.....
A. H. Gill, Massachusetts Institute of Technology, Boston	.....	.....	39.60	.....	.....	.....	34.30	30
A. G. Stillwell, Stillwell Provisioner Laboratory, New York	.....	.....	39.75	25	.....	.....	33.70	25
Stillwell & Gladding, New York	.....	.....	39.50	.....	.....	.....	33.40	.....
Larkin Soap Company, Buffalo, C. W. C	.....	.....	38.76	.....	.....	.....	33.20	.....
Larkin Soap Company, Buffalo, W. W. S	.....	.....	38.92	.....	.....	.....	33.65	.....
Larkin Soap Company, Buffalo, J. C. T	.....	.....	38.95	.....	.....	.....	33.76	.....
Average	39.66	.....	39.51	.....	33.43	.....	33.57	.....
Maximum	40.15	.....	40.20	.....	34.05	.....	34.30	.....
Minimum	39.40	.....	38.72	.....	31.75	.....	32.30	.....
Difference	.75	.....	1.48	.....	2.30	.....	2.00	.....

From the results given in these tables and those obtained under various conditions by different analysts[a] the following conclusions are drawn:

1. The method of preparing the fatty acids for the test is immaterial and the analyst should be allowed to use the method which seems most convenient to him. There is some danger from fire in alcoholic saponification, but this method is quicker and there is less likelihood of incomplete saponification, though, as Mory has shown, this question is not a serious one. A number of chemists have used methyl alcohol and find it equally satisfactory and much cheaper. The alcohol should be completely removed where the alcoholic method of saponification is used. The scheme given in the Dalican method effects this removal completely.

2. The fatty acids should be dry. It seems to the referee that a careful study of the results of this year will prove that the method outlined in the Dalican scheme—i. e., filtering and drying 20 minutes at 100° C—is sufficient and convenient, but does not change the titer.

3. The method of stirring is the chief factor in the difference in titer, and extraordinary care should be taken by the operator to follow exactly the method prescribed, in order that comparable results may be obtained.

4. The Wolfbauer method of stirring gives higher results, especially on fats of a low titer; it gives more uniform results where there is variation in temperature; it is the more scientific and gives more nearly the true titer.

5. There should be a standard thermometer for titer tests, so that all thermometers used for this purpose would have the same size bulb, the same length of stem, and be made of the same kind of glass and thus a stem correction could be accurately applied, or else the thermometers should be standardized under the conditions under which they are used. This latter way would seem to be the more satisfactory.

The associate referee offers the following tentative method for criticism and discussion:

Weigh 75 grams of fat into a metal dish and saponify by using 60 cc of 30 per cent sodium hydrate (36° Baumé caustic soda) and 75 cc of 95 per cent by volume alcohol or 120 cc of water. Boil down to dryness with constant stirring to prevent scorching. This should be done over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water and, if alcohol has been used, boil for 40 minutes in order to remove it. Add 100 cc of 30 per cent sulphuric acid (25° Baumé sulphuric acid) to free the fatty acids, and boil until they form a clear, transparent layer. Collect the fatty acids in a small beaker and place on a steam bath until the water has settled, then decant them into a dry beaker, filter, using a hot-water funnel, and dry 20 minutes at 100° C. When dried, cool the fatty acids to 15° C or 20° C above the expected titer and transfer to the titer tube, which is 25 mm in diameter and 100 mm in length (1 by 4 inches) and made of glass about 1 mm in thickness. This is placed in a 16-ounce, salt-mouth bottle of clear glass about 70 mm in diameter and 150 mm high (2⅝ by 6 inches), fitted with a cork which is perforated so as to hold the tube rigidly when in position. The thermometer, graduated to 0.1° C, is suspended so that it can be used as a stirrer, and the mass is stirred slowly until the mercury remains stationary for 30 seconds. The thermometer is then allowed to hang quietly with the bulb in the center of the mass and the rise of the mercury observed. The highest point to which it rises is taken as the titer of the fatty acids.

The fatty acids are tested for complete saponification as follows:

Three cc of the fatty acids are placed in a test tube and 15 cc of alcohol (95 per cent by volume) added. The mixture is brought to a boil and an equal volume of

[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Circular No. 22.

ammonia (0.96 sp. gr.) added. A clear solution should result, turbidity indicating unsaponified fat. The room temperature must be reported.

The referee had a thermometer made which removes some of the difficulties. It is graduated in one-tenth degrees from 25° C to 60° C and has a bulb which allows the temperature to rise much higher without injury to the thermometer. This instrument can always be immersed in the fat to a definite point and thus the error due to the rising of the mercury column above the liquid will always be the same.

The Belfield Test for Beef Fat in Lard.

Six samples of lard and beef mixture were prepared and sent out by the referee to ten chemists who had experience in making this test, with directions as to the exact details to be followed. The reports from all but two of the collaborators were unsatisfactory, and the referee feels that further work should be done before any report is made, and so would recommend that the work be continued for another year.

The referee found in his work: (1) That a uniform temperature of about 20° C is best suited to give good forms of crystals. (2) That sudden cooling during crystallization produces crystals hard to distinguish from those of beef. (3) If conditions 1 and 2 are observed the addition of lard stearin does not interfere with the value of the test. (4) That lard stearin, if crystallized at a low temperature, gives crystals difficult to distinguish from those of beef.

A large number of photo-micrographs of crystals produced under varying conditions were taken by Mr. B. J. Howard.

In response to the call for the report on the adulteration of dairy products the referee, Mr. Leach, spoke as follows:

REPORT ON ADULTERATION OF DAIRY PRODUCTS.

By A. E. Leach, *Referee.*

Last year a number of additional methods for the detection of milk and butter preservatives and coloring matters, the determination of fat in cheese, and for the examination of condensed milk were submitted to the association and adopted as provisional. This year, owing to pressure of other matters, no specific lines of work were carried out that are ready at present to be reported. Considerable work has been done, however, by Mr. Lythgoe and myself on the detection of watered milk, the results of which, as far as they have been carried, will be found in the October number of the Journal of the American Chemical Society.[a] Heretofore the detection of added water in milk, especially in small amounts, has been largely a matter of guesswork, but by the use of the Zeiss immersion refractometer, working with the milk serum, we have found that definite conclusions may be reached. This instrument is comparatively new.

Incidentally it might be said that, aside from its usefulness for this particular purpose, the immersion refractometer will be found of great value to every analytical chemist. By its use many laboratory reagents of required strength may be readily prepared or standardized, including normal and tenth-normal solutions, and the strength of a wide variety of solutions may be established in a very easy and simple manner.

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[a] 1904, *26:* 1195.

In connection with the work on food adulteration, Mr. Bigelow submitted the following paper for publication:

NOTE UPON A LIMITATION OF THE ARATA AND THE SOSTEGNI AND CARPENTIERI TESTS.

By Wm. Frear and R. O. Brooks.

In the bulletin giving provisional methods for the analysis of food products adopted by this association,[a] the Arata and the Sostegni and Carpentieri methods of wool-dyeing are described under the general caption, "3. Determination of coal-tar coloring matters by dyeing wool." While the first paragraph of the description of the Arata test states that the test was devised for the detection of coal-tar colors added to wines and was later applied by Winton in the examination of fruit products, the language at other points suggests that all these tests are based upon a generic difference between coal-tar dyes, on the one hand, and all vegetable colors on the other. For example, the term "vegetable color" occurs in the line before the last in the description of the Sostegni and Carpentieri method, and "vegetable coloring matter," in the fourth line, fourth paragraph, of the description of the Arata method. The language of the official bulletin in this connection finds parallels in the phraseology employed in other publications.[b] The context in the latter cases shows that the writers had in mind solely the natural colors of wines as compared with the coloring agents employed in wine adulteration.

In a communication received several months ago from H. Kohnstamm & Co., New York, importers of dyestuffs, their chemist, Dr. H. Endemann, noted that there are colors of purely vegetable origin which are dissolved from wool by the action of dilute ammonia, and, upon the acidulation of this solution, impart to wool a deep bright tint. He further said that in States where the use of coal-tar dyes in foods is prohibited, prosecutions had been instituted upon the basis of the results of the Arata test in cases where the coloring matter was distinctively of a harmless vegetable nature. One substance especially cited was archil, used to impart a red or purple color to confectionery. This color, the product of the lichens *Rocella tinctoria* and *R. fusiformis*, is described in respect to its properties as a dye for wool in Hummel's[c] tables; but the description is not sufficiently full as to the solvent effects of dilute ammonia to indicate the probability of its giving the Arata test from the second acid bath.

At the request of the correspondents above named the Arata test was applied by the writers to three samples of archil which were said to have been natural rather than synthetic products; two contained sulphonic acids, the third was free therefrom. The test was, at the same time, applied to commercial litmus, since this dye also is derived from *Rocella* and other lichen genera. In each case a deep, bright dyeing was obtained from the second acid bath.

While the careful tests made upon the coloring matters of fruits conclusively establish the fitness of the improved Arata test to distinguish them from the coal-tar dyes now used to color fruit products, the facts above mentioned show that this test is not generic for vegetable colors as a whole and that collateral investigation is necessary

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[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 65, pp. 111–113.

[b] Compare B. Hass, Zts. anal. Chem., *30:* 502 *seq.;* Bujard and Baier, Hilfsbuch f. Nahrungsmittel-Chemiker, 2d ed., p. 295; Leffmann and Beam, Food Analysis, p. 77, last paragraph, lines 9 and 10.

[c] J. J. Hummel, Dyeing of Textile Fabrics, Cassell & Co., Ltd.; Allen, Commercial Organic Analysis, 2d ed., *3:* (1) 404.

in the case of certain tints to establish the identity of the dye as a coal-tar product instead of a vegetable color of other than fruit origin.

Both the lichen colors tested were found to be very imperfectly dissolved from wool by 1 per cent ammonia water; even after boiling for several hours the wool retains a deep purplish-blue color. Such behavior is sufficiently distinctive to suggest the need for collateral tests before a conclusion is drawn respecting the nature of the dye.

There followed a discussion of the reports on distilled liquors and beer, by Mr. Wiley and Mr. Barnard, which was in part as follows:

Mr. Wiley. Particular attention should be called to the report on distilled spirits, as these, especially whisky and brandy, the best-known spirits, are subject to extensive adulteration, and it is claimed by some that the adulterated article is much better than the straight product. At present we are able to distinguish between the genuine article and the artificial chiefly by the artificial color. However, this point is very important, because an artificial whisky can not be made without artificial color. The rectifier's law legalizes the very adulteration of which we are speaking. The greater part of our whisky, at least 85 per cent, is made by the rectifier. It becomes very important, therefore, that the inspector should be able to detect this article. But a more important problem confronts us. Will it ever be possible for the chemist to distinguish between the artificial essences and ethers and those produced in aging distilled liquors? I do not believe that the solution of this problem is beyond the scope of chemistry and the work of this association. In regard to the report of the associate referee on beer, I would say that at the Chicago exposition it was decided that all beers containing less than 0.5 per cent of protein should be classed as made of malt substitutes, and all containing more than that amount should be considered as made of malt alone. This rule was accepted and acted upon by the jury. I would like to ask the associate referee what percentage of protein he considers should be standard?

Mr. Barnard. The half per cent limit works very well for perhaps the larger class of beers. In some cases, however, malt substitutes could be used to a limited extent without reducing the protein below 0.5 per cent. Therefore, it seems that while the method is satisfactory in throwing out the so-called "temperance beers" it is not always satisfactory with others.

Upon motion by Mr. Wiley the hours for the meeting of the association were fixed at from 10 o'clock to 1 and from 2 until 4.

APPOINTMENT OF COMMITTEES CONCLUDED.

The president announced the following committees:

Committee on resolutions: Messrs. Van Slyke, Snyder, and Fraps.

Committee on nominations: Messrs. Ross, Leach, and Davidson.

Committee on amendments: Messrs. Street, Beal, and Bizzell.

The report on dairy products being in order, it was read by the secretary, in the absence of the referee, as follows:

REPORT ON DAIRY PRODUCTS.

By G. E. Patrick, *Referee.*

On July 27, 1904, the following letter was sent to those chemists who had expressed their willingness to join in the work:

Dear Sir: We learn from Doctor Wiley, secretary of the Association of Official Agricultural Chemists, that you have expressed willingness to join in this year's cooperative work on dairy products.

The present referee was instructed by the association to continue the investigation of the effects of preservatives upon the albumin of milk, with special reference to any interfering action they may exert in the determination of albumin by the official methods. Mr. G. W. Cavanaugh, referee for 1901–02, furnished evidence that formaldehyde in milk, at least when present in quantities somewhat larger than commonly used, causes low results for albumin and that the results are lower as the amounts of formaldehyde are larger or as its action is longer continued. (Proceedings, 1902, Bul. 67, page 37.)

The present referee has verified Mr. Cavanaugh's observations with milks that had received unusually large doses of the preservative. With such samples, both casein and albumin being determined by the official methods[a] the results showed not only a deficit of albumin but also a corresponding increase in the amount of "casein," i. e., proteid thrown down by acetic acid at 40° C. Results were as follows, after correcting for the volume of formalin added:

Effect of formalin on the albumin of milk.

Amounts of 40 per cent formalin added per 400 cc of milk.	Number of days elapsing before analysis.	Nitrogen of casein.	Nitrogen of albumin.
		Per cent.	*Per cent.*
None (Fresh milk)	None.	0.385	0.072 (dups. 0.065 and .079)
1. 0.5 cc	18	.385	.062
2. 4.0 cc	18	.438	.011
2. Same	34	.450	None.
3. 16.0 cc	18	.460	None.
3. Same	34	.476	None.

Unfortunately, by oversight, portion No. 1 was not analyzed after a longer period than eighteen days. At the end of that time it showed only a trifling loss of albumen, if any, and no increase in "casein."

The other portions, Nos. 2 and 3, containing excessive amounts of formaldehyde, showed no albumin in three out of the four analyses made and only a mere trace in the fourth; but the "casein" in each instance approximated the sum of the casein and albumin of the fresh milk. The formaldehyde evidently caused albumin to appear along with the casein. Further work is needed on samples containing only 1 to 2 cc of formalin per liter of milk.

Your referee has also made experiments with $CHCl_3$, $K_2Cr_2O_7$, CS_2, and $HgCl_2$, with results which showed no greater variations from those on the fresh sample than could be charged to error of analysis (possibly excepting those on the samples preserved with $CHCl_3$ and with $HgCl_2$, in both of which the casein came a trifle low and the albumin a trifle high).

If you can take part in the work we would advise you to make experiments with the following preservatives, or with as many of them as you can, in the amounts stated, per liter of well-skimmed milk. (The last two in the list the referee has not worked with.)

[a] This was a mistake as regards albumin. There is as yet no "official" method for albumin in milk. The provisional method was the one here used.

Formalin of about 40 per cent strength, 1 cc and 2 cc per liter.
Chloroform, 30 cc and 50 cc per liter.
Mercuric chlorid 0.5 gram, in very fine powder, per liter.
Potassium bichromate, saturated H_2O solution, 5 cc per liter.
Carbon bisulphid, 20 cc per liter.
Benzol, 50 cc per liter.
Sodium fluorid, 10 and 20 grams per liter.

Samples of milk will not be sent out, as this work can best be done from beginning to end by the individual chemist. He should have the milk fresh and well skimmed; should analyze the fresh milk at the start and the preserved portions at least twice, three times if possible, at intervals of two or three weeks thereafter.

Detection of renovated butter.

In view of the difficulty sometimes experienced by chemists in identifying renovated butter with certainty, it is proposed to include this line of study in the work of the present year. This means merely a continuation of the work done upon this subject in 1900–1901, when Mr. Le Clerc was referee. New directions for making the examinations will, however, be sent out, together with samples of different kinds of butter (including some made from pasteurized cream) immediately upon application from those who wish to take part.

Please notify the referee promptly if you can take part in this work on butter, that he may send you samples and directions without delay.

Send in reports on all the work as soon as completed.

Respectfully,

G. E. Patrick, *Referee on Dairy Products.*
F. W. Woll, *Associate Referee.*

The report of the work done falls under two heads.

I. The Effect of Preservatives upon the Determination of Albumin in Milk.

Owing no doubt to the referee's tardiness in sending out the circular letter, as well as to the unusually early date of this year's meeting of the association, results upon the milk work have been received from only one laboratory, that of the Wisconsin experiment station, the work having been done by F. W. Woll and George A. Olson. Their report is as follows:

REPORT OF F. W. WOLL AND GEORGE A. OLSON, WISCONSIN.

The work was carried out in accordance with your circular of July 27, 1904, with two exceptions, viz, 0.5 gram of mercuric chlorid and 5 cc of potassium bichromate solution per liter were not sufficient to prevent bacterial action, and new experiments with increased amounts of these preservatives were therefore made, viz, 5 grams of mercuric chlorid and 10 cc of potassium bichromate.

The casein was determined according to the official method and the albumin in accordance with the provisional optional method. All samples were kept at room temperature (20° to 25° C). The results have been corrected for the increase in the volume of the samples caused by the addition of the various preserving solutions, except in the case of formaldehyde.

Table I.—*Analysis of original sample of skim milk.*

Total nitrogen.	Nitrogen of casein.	Nitrogen of albumin.
Per cent.	*Per cent.*	*Per cent.*
0.521	0.421	0.052
.523	.409	.052

TABLE II.—*Effect of added preservatives on nitrogen content of milk (Woll and Olson).*

Preservative added.	Beginning of experiment.		Eighteen days later.	
	Nitrogen of casein.	Nitrogen of albumin.	Nitrogen of casein.	Nitrogen of albumin.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Formalin, 40 per cent, 1 cc per liter	0.421	0.051	0.405	0.0490
	.409	.052	.407	.0505
Formalin, 40 per cent, 2 cc per liter	.420	.052	.435	.047
	.420	.052	.430	.044
Chloroform, 30 cc per liter	.412	.0402	.305	.052
	.412	.0402	.312	.052
Chloroform, 50 cc per liter	.417	.036	.305	.0515
	.415	.036	.317	.0525
Mercuric chlorid, 0.5 gram per liter	.403	.036	(a)	.....
	.401	.036		
Potassium bichromate, 5 cc saturated solution per liter	.409	.050	(b)	.....
	.411	.050		
Carbon bisulphid, 20 cc per liter	.415	.047	.417	.047
	.410	.049	.417	.047
Benzol, 50 cc per liter	.415	.047	.334	.0515
	.417	.048	.336	.0515
Sodium fluorid, 10 grams per liter	.400	.036	.294	.0515
	.394	.036	.298	.051
Sodium fluorid, 20 grams per liter	.408	.035	.334	.052
	.421	.035	.334	.052
Mercuric chlorid, 5 grams per liter [c]	.446	.038	.477	.023
	.451	.042	.481	.026
Potassium bichromate, 10 cc saturated solution per liter [c]	.422	.0465	.353	.0465
	.426	.053	.347	.0404

[a] Five-tenths gram of mercuric chlorid was not sufficient to preserve the milk. Eight days after the beginning of the experiment a violent explosion occurred, destroying the sample, doubtless due to the action of gas-forming bacteria. Five grams of mercuric chlorid was used for preserving the second sample.

[b] Five cc of a saturated solution of potassium bichromate was not sufficient to prevent bacterial action; nine days after the experiment started the milk curdled, and on the eighteenth day it was impossible to obtain a uniform analysis sample. The bottle burst the next day and its contents were lost. Ten cc of a saturated potassium bichromate solution was used for preserving the second sample of milk.

[c] The amount of caseo-nitrogen in the original sample of milk used in these two experiments was 0.438 per cent and 0.437 per cent, and of albumin nitrogen 0.059 and 0.056 per cent. The total nitrogen was not determined.

According to the results of previous work done in this line,[a] benzol, chloroform, and sodium fluorid retard the activity of microorganisms, but have only a slight prejudicial effect on chemical enzyms, while formaldehyde and mercuric chlorid repress the activity of enzyms. The data given in the above table indicate that carbon bisulphid also has this effect.

The results obtained in our work came out as might be expected from what is known concerning the action of the various preservatives on the milk enzyms; chemicals not injurious to the activity of enzyms but inhibiting the activity of microorganisms would not prevent the digestion of the casein, and under favorable conditions the per cent of casein found would therefore be less on standing rather than more.

By calculating the per cent of soluble nitrogen from the data obtained eighteen days after the experiment started, dividing the difference between the total nitrogen

[a] Babcock, Russell, and Vivian, Wis. Exp. Sta. Report, 1898, p. 98; Salkowski, Deutsche med. Wochenschr., 1888, p. 16; Arthurs and Huber, Arch. de physiol., 5 (IV, 1892), p. 651; Pavy, Journal of Physiology, 1898, *22;* 391.

and the caseo-nitrogen by the total nitrogen and multiplying the quotient by 100, the following results were found:

	Per cent.
Soluble nitrogen in original milk	20.3
Plus 30 cc $CHCl_3$	40.9
Plus 50 cc $CHCl_3$	40.3
Plus 50 cc benzol	35.7
Plus 10 grams NaFl	43.2
Plus 20 grams NaFl	35.9

It would appear from these results that 10 grams of sodium fluorid were less injurious to the activity of the inherent milk ferment than 20 grams, or than any other preservative added. On the other hand, the amount may not have been sufficiently large to entirely prevent bacterial action.

It will be noted that the only preservative which appeared to affect the determination of albumin nitrogen in our work was the mercuric chlorid, since the other determinations of this component came within the limits of unavoidable errors of analysis.

REPORT OF G. E. PATRICK AND T. C. TRESCOT, WASHINGTON, D. C.

The work presented in the following table (Table III) was done in January and February, 1904. With very few exceptions the figures given are the means of fairly concordant duplicates, only a very few being from single determinations. All results have been corrected for the volume of the preservative added. The milk contained 2.06 per cent of fat.

TABLE III.—*Effect of added preservatives on nitrogen content of milk (Patrick and Trescot).*

Kind and amount of preservative used.	Number of days elapsing before analysis.	Nitrogen of casein.	Nitrogen of albumin.
		Per cent.	*Per cent.*
None. Fresh milk	None.	0.385	[a] 0.072
Formalin (nearly 40 per cent), 1.25 cc per liter	18	.385	.062
Formalin, 10 cc per liter	18	.438	.011
Do	34	.450	None.
Formalin, 40 cc per liter	18	.460	None.
Do	34	.476	None.
Chloroform, 50 cc per liter	21	.330	.094
Do	34	.298	.086
Potass. bichromate, saturated solution, 5 cc per liter	21	.361	.087
Carbon bisulphid, 20 cc per liter	21	.409	.077
Do	34	.407	.065
Mercuric chlorid, 0.5 gram per liter	21	.345	.115

[a] Duplicates on nitrogen of albumin were 0.065 and 0.079.

Remarks.

The above results seem to show that while a small amount of formalin, as 1.25 cc per liter, preserves the milk unchanged and enables the analyst to obtain practically the same results after 18 days as upon the original milk, very large amounts of the same preservative—as 10 cc to 40 cc per liter—do diminish the yield of albumin by the official method of analysis, as Cavanaugh has stated, and at the same time *increase* by substantially the same amount the yield of what would be reported as "casein." In other words, large doses of formaldehyde evidently cause some or all of the albumin of the milk to precipitate along with the casein. The writer had hoped to

verify this by further work before the date of the present meeting, but circumstances have not permitted.

The results obtained with the other preservatives experimented with show only trifling variations from the results on the fresh milk, except in the case of chloroform after 34 days, in which instance the casein nitrogen is certainly lower than can reasonably be charged to error of analysis. This is doubtless due to the action of the milk enzym or enzyms, discovered by Babcock and Russell. Subsequently, at the end of 77 days, when the milk had become curdled, "but only in fine flecks" according to the laboratory notebook, another analysis was made (due care being taken to avoid loss of the curd through adhesion to the measuring pipette), with the result that for the nitrogen of casein there was obtained 0.272 per cent, as against 0.298 per cent 43 days earlier and 0.385 per cent at the beginning, and for the nitrogen of albumin 0.074 per cent against 0.086 per cent 43 days earlier and 0.072 as the mean of duplicates at the beginning (0.079 and 0.065; see Table III). Thus, although the casein has suffered a very considerable loss, the albumin has apparently suffered none, or at most but an insignificant amount. These results are omitted from the table, because the milk was curdled at the time of analysis. The apparent absurdities in the figures for "nitrogen of albumin" may perhaps be due to mere errors of analysis, but may on the other hand have a real significance.

DISCUSSION OF THE RESULTS AS A WHOLE.

As to the effect of formaldehyde, it appears from the work done that while one or two cubic centimeters of 40 per cent formalin per liter of milk do not in 18 days cause any material lowering of the results on albumin, yet when as many as 10 cc per liter are used (and probably less) there is a very marked diminution in the amount of albumin found, with a corresponding increase in the amount of "casein," or what would be reported as such, for apparently the albumin falls low only because a part of it, either by precipitation or by some other change, has been made to appear with the casein. Even with only 2 cc per liter, the figures of Woll and Olson, while exhibiting variations no larger than are quite allowable as unavoidable errors of analysis, still appear to show this effect of formaldehyde in a very slight degree. There is, however, need of further work along this line, both to verify the tentative conclusions above stated and also to fix with certainty the proportion of formaldehyde allowable in the preservation of milk samples in which casein and albumin are to be determined.

Chloroform, at the rate of 50 cc per liter of milk, was found in both laboratories to permit a very considerable destruction of casein in 18 to 34 days, while the albumin did not appear to suffer at all, and even at the end of 77 days in the Washington laboratory, although the milk had undergone incipient curdling, or curdling of a peculiar kind, the result for albumin was still as high as the mean result obtained on the fresh milk.

Potassium bichromate, 5 cc of a saturated aqueous solution per liter, was sufficient to preserve milk without serious change for 21 days in winter weather (January and February, Washington laboratory), but quite insufficient in summer weather (Wisconsin laboratory). Even 10 cc per liter under summer conditions appeared insufficient to prevent a very material loss of casein in 18 days, while albumin suffered but trifling loss, if any.

Carbon bisulphid, 20 cc per liter of milk, in the work of both laboratories appeared to effect a perfect preservation from both organized and unorganized fermentive agents, since neither casein nor albumin suffered any loss in periods of 18 and 21 days, respectively, and no material loss, if any, even in 34 days in the work of the Washington laboratory.

Mercuric chlorid at the rate of 0.5 gram per liter of milk was a complete failure in the Wisconsin laboratory, the flask exploding from the formation of gas after 8 days,

while in the Washington laboratory the same amount of this chemical preserved the milk so well that in 21 days there was only a very small loss of casein, if any, and no loss whatever of albumin—in fact, curiously enough, the figure obtained for nitrogen of albumin was exactly as much too high (0.04 per cent) as that for casein nitrogen was too low. Whether any gas was formed was not observed. The difference of the results at the two laboratories, here as with potassium bichromate, was doubtless due to the different seasonal conditions. Evidently the amount of mercuric chlorid recommended by the referee is not enough; probably 1 or 1.5 grams per liter will prove sufficient. The figures from the Wisconsin laboratory, where 5 grams per liter were used, certainly appear to indicate that that amount of mercuric chlorid has the same effect as excessive doses of formaldehyde—namely, to increase what is reported as "casein" at the expense of the albumin. While this indication may possibly be due to mere chance, still the point should be kept in mind for future observation.

Benzol and sodium fluorid were worked with only in the Wisconsin laboratory. Fifty cubic centimeters of benzol per liter of milk did not prevent a very material loss of casein in 18 days, while there was no apparent loss of albumin; and 20 grams of sodium fluorid had about the same effect, the numerical results for the two being almost identical at the end of the time stated.

It is thus seen that in this year's work the only preservatives that proved reasonably satisfactory, in the proportions used, for the keeping of milk sample 18 to 21 days where both casein and albumin are to be determined, were carbon bisulphid, 20 cc per liter of milk, and formalin (40 per cent) $1\frac{1}{4}$ to 2 cc per liter. A larger amount of formalin can not be recommended at present, since quantities considerably larger seriously vitiate the results. Of the two preservatives named, carbon bisulphid at present appears to be the safer.

In leaving this part of his report the referee deems the following facts deserving of special mention:

(1) In this year's work every instance in which albumin in the sample preserved for 18 to 34 days came out decidedly low, the "casein" was high by a nearly corresponding amount.

(2) These cases are only those in which what may, I think, be properly called excessive amounts of formalin or of mercuric chlorid were used, the indication being that these agents, used in excessive quantities, so change a part of the albumin that it appears in analysis along with the casein.

(3) In every case where the *casein* came out low—and this occurred wherever the preservative was inefficient either in its nature or from being used in insufficient quantity—the albumin remained practically unchanged (in some cases it even appeared to be a trifle higher than in the original milk, but this may easily have been due to errors of analysis).

These facts apparently mean that preservatives which are not altogether efficient against all kinds of fermentive action protect the albumin much better than they do the casein. But evidently this effect may easily be only apparent, since both may suffer change and a compensation occur for the albumin. However this may be, the facts are suggestive, and it remains to be seen if they will repeat themselves in another year's work.

II. Methods for the Detection of Renovated Butter.

In the circular letter of July 27 it was announced that samples of butter of different kinds would be sent, upon application, to any chemist desiring to join in the work, with directions for making the examinations. Seven applications were received and the samples duly sent, each set of samples comprising the following varieties of butter:

No. 1517. Pasteurized butter, purchased in 1-pound prints.

No. 1519. Renovated butter, purchased in 1-pound prints.

No. 1520. Dairy butter, made from gravity cream, purchased in ½-pound prints from market wagon in Center Market place, Washington. The lot was from one dairy and supposedly from one churning.

No. 1521. Dairy butter, made from gravity cream, packed in crock, and purchased from market wagon in Center Market place, Washington. It was supposed to be from one churning.

No. 1523. Pasteurized butter, so alleged; purchased in 1-pound prints. "Guaranteed" pasteurized.

No. 1525. Creamery butter, not pasteurized. Tub butter.

The directions for examining the samples, printed as Circular No. 19, Bureau of Chemistry, were as follows:

Melting test.

Put some of the butter in a test tube or narrow beaker and heat in the boiling-water oven—or, to obtain the clearest possible results, in an oven at 60° to 70° C. Observe after one-half hour to one hour.[a] Renovated butter always melts turbid, while nearly all genuine butters melt with a clear fat. If they are very much broken down by age, the fat will sometimes be a little cloudy; seldom if ever turbid.

NOTE.—Samples that have been melted and shaken while cooling, in preparation for analysis, will nearly always melt turbid.

Boiling test.

Perform this test in the usual manner with a dessert or table spoon, or with a test tube in the manner described in the Proceedings of the Eighteenth Annual Convention of the Association of Agricultural Chemists, 1901,[b] using butter to the depth of 1¼ inches when melted in the 6-inch test tube.

Oleomargarine and renovated butter yield very little, if any, foam and boil with a crackling sound, while genuine butter yields foam in greater or less abundance (very aged butters, or ladled butters, yield usually the more moderate amounts) and boil, if not "quietly," at least with absence of the crackling sound.

Microscopic examination.

[Magnification about 85 diameters.]

Mounting.—Place the volume of one to two pinheads of butter from a freshly cut surface upon a slide and press it out quite thin under a cover glass, avoiding any lateral motion. Put three or four such mounts upon the slide; and, since the particles of butter are so small, it is better to study at least six mounts, two slides, in order to get true results.

(*a*) *Light field.*—Observe as to smoothness or roughness; as to the abundance, size, and color of the casein spots, if any are seen. Observe whether they are mostly dry or inclosed in water globules. Report any other appearances observed.

(*b*) *Dark field* (light from below screened off).—Observe the casein spots, whether appearing white and gelatinous or white and glistening. (This last is seen in some pasteurized butter.)

(*c*) *With polarized light, nicols crossed.*—Look for fat (or fat-acid) crystals, perfect or imperfect. The latter designate as flakes, frostiness, or haziness, according to appearance.

(*d*) *With polarized light and a selenite plate, blue and yellow, below the stage.*—Observe colors on the blue field. Purple (or violet-red, perhaps) is nearly always seen with rancid butter of whatever kind. Fresh renovated butter may or may not show it. Therefore this color signifies nothing of importance. Its presence or absence should, however, be reported to indicate the condition of the butter. Look for other colors in connection with any supposed fat crystals that may have been discovered with the crossed nicols alone. Red, pink (or flesh color), brass-yellow, and green may in such cases appear on the blue field.

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[a] The precaution not to shake the tubes during the process of the test should have been inserted here, for, as is known to every chemist who has worked much with butters, even a very little shaking during melting will give rise to a turbid fat with any kind of butter.

[b] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 67, p. 115.

(*e*) Place the slide in an oven at 60° to 70° C for five to ten minutes and examine immediately, with plain light, with and without substage illumination—i. e., in "light field" and "dark field" as these terms are used above.

Observe the condition of the curd—whether it is in straggling, moss-like, or fleecy forms (the latter showing only fine particles in the dark field) or in circles; or whether it is in dense, solid masses, and the size of same.

NOTE.—This mode of observation (e) appears to give all the information that is furnished by the Hess and Doolittle "curd test," with more certainty and less work.

The Waterhouse test, modified.

Follow the method as given in the Proceedings of the Eighteenth Annual Convention of the Association of Official Agricultural Chemists, 1901,[a] and in the Proceedings of the Twentieth Convention, 1903.[b]

As teaspoons vary in size, it should be stated that about 8 grams is the amount of butter intended by the words "a slightly rounded teaspoonful."

Not only the main result, i. e., whether or not gathering took place, should be reported, but also (1) the number of minutes before gathering occurred; (2) the temperature of the water in the pan and of that in the cup at the moment of gathering or at the end of ten minutes if gathering did not occur; (3) the appearance of the butter, whether oily or not, as it lies upon the warm water before the stirring is begun.

NOTE.—At least some pasteurized butters (butters made from pasteurized cream) gather in the test, but are slower in gathering than are renovated butters as a rule; and they do not present the oily appearance before stirring.

In an accompanying letter the collaborators were requested to report "all the details of every observation made in the several tests given, as it is important to know how closely different observers can agree in making the observations upon which conclusions must be based."

REPORTS OF COLLABORATORS.

Reports were received from only two collaborators in time to be included bodily in the referee's report sent to the meeting of the association, and from two others later. Therefore all comparison and tabulation of results have of necessity been made since the date of the meeting, as well also as certain experimental work by the referee which seemed desirable in view of some disagreement in results and because of the previous omission by him of some of the tests.

The collaborators who sent in reports are: C. P. Moat, chemist of the Vermont State Board of Health, Burlington; C. A. Crampton, chemist of the United States Treasury, Washington, who writes that the work reported should be credited to Mr. F. D. Simons; J. A. Sewall, chemist of the Bureau of Health of Denver, Colo.; and F. W. Woll, associate referee, chemist of the Wisconsin experiment station, Madison.

The melting test.

The results of the melting test are given in Table IV.

TABLE IV.—*Melting test—Butter melted at 60°–70° C; appearance of fat after one-half to one hour at that temperature.*

Observer.		No. 1517. Pasteurized creamery.	No. 1519. Renovated.	No. 1520. Dairy, from gravity cream.
C. P. Moat		Clear	Turbid	Slightly clouded.
F. D. Simons		do	Very turbid	Slightly cloudy; almost clear.
J. A. Sewall			Turbid	Clear.
F. W. Woll		Fairly clear	do	Rather turbid.
G. E. Patrick	July 20–28	Clear	Very turbid	A little cloudy; not turbid.
	Nov. 11	Clear	do	Moderately turbid; worse than cloudy.

[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 67, p. 127.

[b] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 81, p. 81.

TABLE IV.—*Melting test—Butter melted at 60°–70° C; appearonce of fat after one-half to one hour at that temperature*—Continued.

Observer.		No. 1521. Dairy, from gravity cream.	No. 1523. Pasteurized creamery.	No. 1525. Creamery, not pasteurized.
C. P. Moat		Slightly clouded	Clear	Clear.
F. D. Simons		Slightly cloudy; almost clear.	do	Do.
J. A. Sewall		Turbid		Do.
F. W. Woll		do	Fairly clear	Do.
G. E. Patrick	July 20–28	Clear	Clear	Do.
	Nov. 11	Decidedly turbid; more so than No. 1520.	do	Do.

The results on the several butters by the different observers in the melting test (Table IV) agreed generally very well excepting on sample 1521, where the reports range from "clear" to "turbid." This seemed so surprising that the writer repeated the test, not only on this but on all six samples, on November 11 (when this report was being prepared), with the result that while Nos. 1517, 1523, and 1525 melted clear and 1519 densely turbid, exactly as they had done 100 to 110 days earlier, No. 1520 melted "moderately turbid—worse than cloudy"—and No. 1521 "decidedly turbid—more so than 1520." These results, which are all given in the table, show that the two dairy butters made from gravity cream suffered some change during the 3½ months' storage in the refrigerator which caused a change in their behavior in the melting test, while the creamery butters, pasteurized or unpasteurized, suffered no such change—or not to such an extent as to modify their behavior in this test.

So great a change in the behavior of the dairy butters in so short a time was a great surprise to the referee. In the directions sent out it was stated that in testing butters which are "very much broken down by age the fat will sometimes be a little cloudy, seldom if ever turbid." This statement was in accordance with the writer's experience up to that time, but from the facts here developed it seems that long before they are very badly broken down dairy butters made from gravity cream may yield not only a "cloudy" but even a decidedly "turbid" fat in the melting test; so that, in all probability, the disagreement among the results reported on samples No. 1520 and No. 1521 is due to the samples having been tested at different stages of rancidity by the different observers.

These conclusions, of course, need to be verified by repetition, and especially with samples of which we have absolute knowledge in respect to purity and details of manufacture. Only such samples will be used in next year's work.

The boiling test.

The results by this test are given in Table V. Mr. Woll was unable to report upon this and the microscopic tests, because of other duties.

TABLE V.—*Boiling test.*

Observers.	No. 1517. Pasteurized creamery.	No. 1519. Renovated.	No. 1520. Dairy, from gravity cream.
C. P. Moat (using test tube)	Quietly, with foam	Much noise, no foam.	Noisily, no foam.
F. D. Simons (using test tube)	Quietly, but little foam.	Bumps, no foam	Quietly, some foam.
F. D. Simons (using spoon)	Quietly, abundant foam.	Sputters, no foam	Do.
J. A. Sewall		Decided crackling, no foam.	No crackling, much foam.
G. E. Patrick (using test tube)	Quietly, abundant foam.	Crackling, almost no foam.	Quietly, rather scanty foam.

TABLE V.—*Boiling test*—Continued.

Observers.	No. 1521. Dairy, from gravity cream.	No. 1523. Pasteurized creamery.	No. 1525. Creamery, not pasteurized.
C. P. Moat (using test tube)	Quietly, with foam	Some noise, little foam.	Some noise, much foam.
F. D. Simons (using test tube	Like No. 1520	Quietly, good deal of foam.	Like No. 1523.
F. D. Simons (using spoon)	do	Quietly, abundant foam.	Like No. 1525.
J. A. Sewall	Crackling, very slight foam.		No crackling, much foam.
G. E. Patrick (using test tube)	Quietly, abundant foam.	Quietly, very abundant foam.	Quietly, very abundant foam.

The results with the boiling test, by the four observers, agree substantially on samples 1519 and 1525, and show only minor differences on 1517 and 1523, while on 1520 and 1521, the two dairy butters, one observer in each case reports a behavior which would indicate that the samples had been renovated. The small discrepancies and variations in form of report on the first-named four samples can reasonably be attributed, in large part at least, to the use of different words in describing the same thing seen. But the large discrepancies in the reports on the two dairy butters—one being reported by a single observer as boiling "noisily, with no foam," and the other, by another observer, as "crackling, with very slight foam," while in each case the other three observers obtained results quite different, certainly not indicating a renovated butter—these discrepancies can not be explained by the writer. Possibly more experience in performing the test will enable us to obtain more concordant results.

Microscopic examination.

The results by microscopic examination are exhibited in Table VI.

TABLE VI.—*Microscopic examination.*

No. 1517.—PASTEURIZED.

Observers.	Light field.	Dark field.	Polarized light, crossed nicols.	Selenite plate.	Melted on slide at 60°–70° C. Appearance of curd.
C. P. Moat	Normal	Normal	Nothing	Purple on blue field	Mosslike forms.
F. D. Simons	Smooth; abundant casein, yellowish brown, dry		Slightly hazy		Fleecy forms, light gray in color.
G. E. Patrick[a]	Nearly smooth; many small dark spots of casein.	Many small casein spots, white and glistening—not gelatinous.	Nothing	Solid colors	Fleecy forms, fine particles and circles; a few imperfect straggling forms; no coarse curd.

[a] Prints *a*, *b*, and *c* on July 29, Oct. 15, and Nov. 30, repectively, gave same results, save that *c*, on Nov. 30, showed white flakes with the crossed nicols, giving colors with selenite.

No. 1519.—RENOVATED.

C. P. Moat	Many casein spots, large and small, dirty yellow, mostly dry.	Much casein; gelatinous	Nothing	Fat crystals, variegated colors.	Small solid pieces of curd.
F. D. Simons	Rough; moderate amount of casein, dark dirty brown, inclosed.		Hazy		Dense brownish yellow; inclosed.
G. E. Patrick	Rough; many casein spots, large and small, yellow. About half are dry and half are inclosed in water globules.	Many casein spots, large and small, gelatinous.	Nothing	July 19, solid colors; July 27, purple mottling on blue field.	All the curd is in coarse, solid particles.

No. 1520.—DAIRY FROM GRAVITY CREAM.

C. P. Moat	Very few small casein spots, pale yellow.	Few casein spots; gelatinous.	Nothing	Slight purple	Straggling forms.
F. D. Simons	Smooth; scanty casein, yellowish brown, dry.		Marked haziness		Fleecy or mosslike forms, gray.
G. E. Patrick	Not very smooth; H_2O globules conspicuous and irregular in size; rarely a small casein spot, pale yellow.	Many minute casein spots, gelatinous.	Different trials gave nothing, light hazy, and frostiness.	Faint purple on blue field.	Mosslike and fleecy forms, fine particles and circles; no coarse curd.

No. 1521.—DAIRY FROM GRAVITY CREAM.

C. P. Moat	Normal	Normal	Nothing	Slight violet red	Straggling forms.
F. D. Simons	Moderately smooth; moderate amount of casein, light yellowish brown, dry.		Frosty		Abundant, fleecy, or mosslike forms, gray.
G. E. Patrick	Smooth, save for numerous pale yellow casein spots, large and small, most of them dry; somewhat resembles renovated butter.	Many casein spots; gelatinous.	Different trials gave nothing, and a little frostiness with rarely a flake.	Different trials gave solid colors and faint purple on blue field.	Nearly all in mosslike and fleecy forms and circles; a few coarse pieces of solid curd, but the appearance could not be mistaken for that of renovated butter.

No. 1523.—PASTEURIZED.

C. P. Moat	Normal	Normal	Nothing	Solid colors	Mosslike, straggling forms.
F. D. Simons	Smooth; moderate amount of casein, yellowish brown, dry.		Slightly hazy		Fleecy or mosslike, gray.
G. E. Patrick:					
Print *a* (July 26)	Not very smooth; many small opaque particles of casein.	Many minute casein spots, as a rule not really gelatinous, somewhat glistening.	Nothing	Solid colors	Some straggling forms, but curd is mostly in fleecy forms and circles; no coarse curd.
Prints *x*, *c*, and *d* (August and October).	Smooth; very rarely a casein spot, pale yellow.	A few casein spots, gelatinous or semigelatinous.	do	do	All in fleecy, mosslike, and straggling forms and in circles; no coarse curd.

No. 1525.—CREAMERY, NOT PASTEURIZED.

C. P. Moat	Normal	Normal	Nothing	Solid colors	Straggling, mosslike forms.
F. D. Simons	Smooth; abundant casein spots, yellowish brown, dry.		do		Mosslike; gray.
G. E. Patrick	Rarely a very small casein spot, pale yellow.	Moderate number of small casein spots, mostly very minute in size; gelatinous.	do	Solid colors; four months later faint purple mottling on blue field.	All in mosslike forms; no coarse curd.

Comparison of the results of microscopic examination by the different observers reveals in general a most gratifying agreement in respect to the important points. Exceptions to this are very rare, and the clearness with which the renovated butter (No. 1519) is distinguished from all the others serves to emphasize the great value of the microscope in this line of work. The test proposed by the referee, namely the observation of the *form* of the curd after the mounts have been melted on the slide at 60° to 70° C, gave useful results in the hands of all three observers.

The peculiar appearance of the casein of the pasteurized butter, No. 1517, observed by the referee in the dark field, namely a *glistening* instead of a gelatinous appearance, was observed by him, though in a less marked degree, on a sample print (obtained for examination prior to the purchase of 8 prints more) of the alleged pasteurized butter, No. 1523, but could not be recognized in three prints of the eight, examined after the samples had been sent to the collaborators. (See Table VI.) Also, the appearance after melting on the slide at 60° to 70° was different. For these reasons, and others mentioned under the Waterhouse test, the referee is by no means certain that all, or any, of the samples of this butter sent out were really made from pasteurized cream. No more is he certain that it was not, so little is at present known concerning means of identifying this kind of butter. Such uncertainty concerning the character of the samples must be avoided in future work.

The Waterhouse test, modified.

The results by this test will be reported in the following order:

No. 1525. Creamery butter, not pasteurized. Tub butter. Table VII.
No. 1517. Pasteurized butter (creamery). In prints. Table VIII.
No. 1523. Pasteurized butter (alleged). In prints. Table IX.
No. 1519. Renovated butter. In prints. Table X.
No. 1520. Dairy butter, made from gravity cream. In prints. Table XI.
No. 1521. Dairy butter, made from gravity cream. In crock. Table XI.

Most of the referee's work with this test has been done since the meeting of the association for the reasons (1) that he was unable to do more than a very little of it earlier, and (2) that certain disagreements between the results of different observers—chiefly between those of himself and others—and between his own results at different times, seemed to call for considerable repetition of work. As the results of such repetition at later dates, in case of the pasteurized butters, seemed to indicate at least the possibility that the age of such butters may affect their behavior in the Waterhouse test, the referee has thought it desirable to give the date of each trial or test, along with his results in the tables; and this he has done not only for the pasteurized butters but for the others also.

TABLE VII.—*Waterhouse test modified—Sample No. 1525, creamery tub butter, not pasteurized.*

Analyst.	Time stirred.	Result, gathered or granulated.	Final temperatures.		Appearance when melted, before stirring.
			In pan.	In cup.	
	Minutes.		°C.	°C.	
C. P. Moat	10	Granulated	17½	17½	Not oily.
F. D. Simons	10	....do			Granular.
	20	....do	14	16	
F. W. Woll[a]	10	....do	15.3	15.6	Not oily.
G. E. Patrick:					
Oct. 7	10	....do	15½	16	Do.
Do	10	....do	15½	16	Do.
Nov. 4[b]	10	....do	18	18	Do.

[a] Used glass beaker instead of tin cup.
[b] Initial temperature of water in pan was 11° instead of 12°.

The reports on the unpasteurized creamery butter, No. 1525 (Table VII), are all in perfect accord with respect to the main result, as was to have been expected, the only difference being with respect to the final temperatures—differences which in this instance evidently had no influence upon the results. In order to see if this butter could be made to "gather" by a moderate elevation of temperature in the test (this sometimes being the effect of such change), the referee made one test with the initial temperature of the water in the pan 14° instead of 12° C; but the result was unchanged, as shown in the table.

TABLE VIII.—*The Waterhouse test, modified—Sample No. 1517, pasteurized creamery butter in prints.*

Analyst.	Time stirred.	Result, gathered or granulated.	Final temperatures.		Appearance when melted, before stirring.	Remarks.
			In pan.	In cup.		
	Minutes.		° *C.*	° *C.*		
C. P. Moat	10	Granulated	16	16½	Not oily	
F. D. Simons	10	do			Granular	
	12 to 14	Part gathered in granular lump.	14	16		
F. W. Woll	10	Granulated	15	16	Not oily	Used glass beaker instead of tin cup.
G. E. Patrick:						
June 29. Print *a*	8½	Gathered in a firm lump.	18	18½	do	
Oct. 14. Print *b*	10	Granulated	16½	16½	do	Repeated same day, same result.
Nov. 7. Print *c*	10	do	16	16½	do	
Do	10	do	17¼	17¾	do	Initial temperature in pan was 14° vice 12°.
Do	10	do	18½	18½	do	Initial temperature in pan was 15° vice 12°.

The only discordant result among the reports on pasteurized butter, No. 1517 (Table VIII), is that obtained by the referee with one of the prints, designated here as print *a*, on June 29, the day the butter was purchased. This test was supposed to verify the printed statement that the butter was made from pasteurized cream, since fresh creamery butter made from pure unpasteurized cream does not "gather" in the Waterhouse test. This disagreement between his result of June 29 and the results obtained by the three other observers at dates certainly later than August 15 led the referee to repeat the test. This he could not do upon print *a*, which had not been saved, but the test was again applied to the two other prints, here designated as *b* and *c*, which had been purchased in the same 10-pound lot with print *a* and which were without doubt exactly the same kind of butter, showing as they did the same peculiar appearances of the casein in the light and dark fields of the microscope that print *a* had previously shown, as well as the practical absence of moss-like and straggling forms of curd after melting on the slides at 60° to 70° C. As shown in the table, the results were quite different from the earlier one; both "granulated," like ordinary creamery butter, instead of "gathering" during the 10 minutes' stirring as print *a* had done, when the butter was fresh. They did gather in firm lumps at the end of 15 minutes' stirring, by cohesion of the granules, but there are few data for comparison, as the test is not usually continued so long.

It was noticed that the final temperature in the referee's test on June 29 was about 2° higher than that in the tests by the other observers—due no doubt in part to dif-

ferences in room temperature—and it was thought that this might possibly account for the difference in results. Therefore two additional tests were made on print *c* November 7, with the initial temperature of water in the pan respectively 14° and 15° instead of 12°. The final temperature was thus brought as high as that in the test of print *a*, but the results were still different, as recorded in the table (VIII). Print *c* in November persistently granulated in the test, while print *a* on June 29 was recorded as having "gathered in a firm lump in 8½ minutes." Thus, if we assume all the prints to have been originally alike—and this assumption is supported by the microscopic observations recorded in Table VI—it is clearly indicated that unless the referee made an error in his work of June 29 the disagreement between that result and those of the three other observers was caused by some change occurring in the butter in the interval between the date of his work and the date or dates of theirs (August 15 to September 20). It is believed that the butter in question was of uniform make, all being pasteurized, and that all the prints of this lot were substantially alike, and the referee is inclined to accept, tentatively, of course, the explanation that a pasteurized butter which when fresh will gather in the Waterhouse test (modified) may, after a few weeks or months of storage, granulate in the test, like an ordinary creamery butter. This view receives some degree of support also from the results on the other alleged pasteurized butter, sample No. 1523, of which the record in the Waterhouse test (Table IX) is almost exactly the same as that of No. 1517, just reported.

TABLE IX.—*Waterhouse test, modified—Sample No. 1523, alleged pasteurized creamery butter in prints.*

Analyst.	Time stirred.	Result, gathered or granulated.	Final temperatures.		Appearance when melted, before stirring.	Remarks.
			In pan.	In cup.		
	Minutes.		°*C.*	°*C.*		
C. P. Moat	10	Granulated	16	16½	Not oily	
F. D. Simons	10	do			Granular	
	20	do	14	16		
F. W. Woll	10	do	15½	17	Not oily	Used glass beaker instead of tin cup.
G. E. Patrick:						
July 26, print *a*	7½	Gathered in soft lump.	17½	18	do	
Oct. 13, print *b*	10	Granulated	16¾	17	do	Repeated same day, same result.
Do	10	do	18	18	do	Initial temperature in pan was 14° vice 12°.
Oct. 14, print *c*	10	do	16¼	16¾	do	Repeated same day, same result.
Oct. 14, print *d*	10	do	16¾	17	do	Do.

A perusal of the results on the alleged pasteurized butter, No. 1523 (Table IX), shows that here again, as with No. 1517, the only discordant result was that obtained by the referee on the first print tested by him, designated in the table as print *a*. This print was tested as a trial sample before purchasing 8 pounds more of the same lot, the prints of this lot having all been made, it was alleged, from the same tub butter by the local dealer. The result of the test was accepted as verifying the verbal and printed statement that the butter was made from pasteurized cream. By the appearances under the microscope also this print was found to be measurably in line with the pasteurized butter No. 1517, a brand of butter which the referee had convinced himself was actually what it purported to be. And the similarity was equally

apparent in the Waterhouse test, as stated. Print *a* of both butters, tested by the referee when they were entirely fresh, gathered in 8½ and 7½ minutes, respectively, while other prints tested at later dates, whether by the other observers or by the referee, in every case granulated like ordinary creamery butter. So here again, with No. 1523 as with No. 1517, there are three possible explanations—(1) faulty work by the referee; (2) change in properties of the butter by keeping; and (3) difference in the original character or properties of the different prints. In the case of sample 1517 this last explanation was rejected because three different prints gave identically the same appearances in the microscopic test (except for such appearances as we know come with age). (See Table VI.) But in the case of No. 1523 an examination of three prints left over, after the distribution of samples to collaborators, gave appearances not exactly like those previously obtained with print *a*—the difference being particularly marked in the "light field" examinations, and less so in the examinations of the curd after the mounts had been melted on the slide at 60° to 70° C. Thus it appears possible that in this case there was a difference in the original character or properties of the different prints; that the first print examined by the referee was made from pasteurized cream while the balance, delivered later, were not; or that the latter were from cream pasteurized at a lower temperature or for a shorter time. But, while this is a possibility, it is perhaps more reasonable to accept tentatively one of the other possible explanations, viz, (1) faulty work by the referee, or (2) a change in the behavior of the butter by keeping. And in this state of uncertainty the referee is obliged to leave the matter until further work upon samples, whose character and mode of manufacture are known absolutely, shall throw more light upon the subject.

TABLE X.—*Waterhouse test, modified—Sample No. 1519, renovated butter.*

Analyst.	Time stirred.	Result, gathered or granulated.	Final temperatures.		Appearance when melted, before stirring.	Remarks.
			In pan.	In cup.		
	Minutes.		°C.	°C.		
C. P. Moat	6½	Gathered	16½	17	Oily	
F. D. Simons	10	do	14	16	do	
F. W. Woll	8	do	14.8	15.8	do	Used glass beaker instead of tin cup.
G. E. Patrick, four trials, Sept. 22–Oct. 4.	*a* 4½ to 8	Gathered in soft, flat mass (not a lump).	16.5 to 17	17 to 18	do	

a The times recorded are 4½, 4½, 5½, and 8 minutes. The last is probably due to inadvertent waiting for a true lump to form, which in this case would not occur until long after the fat had gathered in a soft mass.

The reports from the several observers on the renovated butter (No. 1519, Table X) agree perfectly as to the general result, differing only in regard to the time required for the result to become evident. And the disagreement on this point is no doubt mainly due to the fault of the referee in so often using the phrase "gathering in a lump" and neglecting to say that the gathering may also be in the form of a *soft mass*, too nearly fluid to take the form of a lump. Had this been stated in the circular sent out, the reports on the time required for gathering would in this instance probably have ranged between 4½ and 6 minutes. (See footnote to Table X.)

TABLE XI.—*Waterhouse test, modified—Samples No. 1520 and No. 1521—Dairy butters made from gravity cream.*

SAMPLE 1520—IN PRINTS.

Analyst.	Time stirred.	Result—gathered or granulated.	Final temperatures.		Appearance when melted, before stirring.	Remarks.
			In pan.	In cup.		
	Minutes.		°C.	°C.		
C. P. Moat	9	Gathered	16⅛	17⅛	Oily	
F. D. Simons	10	Granulated			Granular	
	14	Gathered in granular lumps.	14	16		
F. W. Woll	10	Granulated	15.7	17	Not oily	Used glass beaker instead of tin cup. Initial temperature in pan slightly above 12°.
G. E. Patrick:						
3 trials on print *a*, Oct. 1 to 4.	10	.....do	16¼	16⅜	Not oily, but shows oil globules.	
4 other trials on same print, same dates.	6–9	Gathered in firm lump or lumps.	16¼–17⅛	16¼–17⅜	.....do	In one trial the initial temperature in pan was 12⅛°, in another 13° instead of 12°.
3 trials on print *b*, Oct. 1.	10	Granulated	16¾–17½	16¾–17⅝	.....do	Do.
2 trials on print *c*, Oct. 4.	10	.....do	16⅝	16½	.....do	

SAMPLE 1521—IN CROCK.

C. P. Moat	10	Granulated	16	16⅛	Not oily	
F. D. Simons	10	.....do			Granular	
	12	Small granular lump	14	16		
F. W. Woll	10	Granulated	15	16.3	Not oily	Used glass beaker instead of tin cup.
G. E. Patrick:						
Oct. 1	10	.....do	17⅛	17½	.....do	Initial temperature in pan was 12⅛° instead of 12°.
Oct. 7	7	Gathered in a firm lump after having first granulated.	16	17	.....do	
Do	7	Gathered in a soft lump after having first granulated.	16	16¾	.....do	
Oct. 8	10	Granulated	16	16½	.....do	Duplicate tests on portion from bottom of a bottled sample, bottled about Aug. 1.
Do	10	.....do	16½	16⅝	.....do	
Do	10	.....do	16⅝	16⅝	.....do	Duplicate tests on portion from top of same bottled sample.
Oct. 13	10	.....do	16¼	16½	.....do	

In Table XI are the results on the two dairy butters (Nos. 1520 and 1521) made from gravity cream; and here we meet with a few disagreements, both between the results of different observers and between those of the same observer in different trials. With both of these butters it is evident that a very slight variation in the conditions of the test is liable to change the result entirely. A similar fact has been observed repeatedly with respect to dairy butters, at least such as are sold from country wagons in the markets of Washington, but the reason for it has never been ascertained. However, the gathering of such butters, when it occurs, seldom if ever resembles that of renovated butter.

If we can secure for next year's work samples of fully authenticated pasteurized butter, with details of manufacture, and of gravity cream butter of known history our work with the Waterhouse test will be more satisfactory, if not more instructive, than it has been the present year.

Recommendations.

It is recommended—

1. That the two lines of work of this year be continued for another year.
2. That the referee for next year be requested to study the methods of determining sugars in condensed milks and milk powders or dried milks.

Mr. Wiley. I would like to call attention to a peculiar butter case that came to my notice. In northern Europe the butter is uncolored, but as you go south the color deepens and in the far south it is red. A shipment of butter to Martinique, which was inspected, was condemned on the ground that the butter fat was not pure. The sample was perfectly red and contained about 38 per cent of butter fat, the remainder being water, salt, and coloring matter. It developed that in Martinique this butter is used in making sauces, etc.; that 4 to 8 per cent of annatto is added to it, and that it is never used until it has been exposed to the rays of the sun for some time. In this special case we decided that the product was not butter.

In the absence of the referee on insecticides his report was read by the secretary, as follows:

REPORT ON INSECTICIDES, FUNGICIDES, AND DISINFECTANTS.

By Bernard H. Smith, *Referee.*

It is but five or six years since the first referee on insecticides and fungicides was appointed, yet during this period great progress has been made in their analysis, this being particularly true of that most important group of insecticides, the arsenicals. Enormous harm may be accomplished by the unchecked ravages of injurious insects, remarkable alike for their capacity for food and their rapidity of multiplication. The association chemists, realizing the responsibility resting upon them, have developed volumetric methods of analysis, which from the standpoint of both rapidity and accuracy are a great improvement over those used a decade ago. Paris greens have been studied until now by means of a better knowledge of their physical structure and breaking-down properties we are better able to understand the varying peculiarities of their effect; also, additional light has been thrown upon the composition of London purple, a subject of considerable annoyance to investigators in times past.

By the action of the last meeting of the association there was added to the work of the referee on insecticides and fungicides another important and closely allied

class of compounds—that of disinfectants. This step was made necessary by the recent general realization of the value of sanitary measures as a factor in enhancing the comfort and safety of the people, which is evidenced by the remarkable growth of public-health movements. The latter has naturally produced a great increase in the use of disinfectants. It is essential that these compounds should be analyzed by exact, and, if possible, uniform methods, by those who rely upon their effectiveness in combating disease, for in the hands of an unprincipled dealer they are especially subject to great variations in strength and therefore in germicidal value.

I. Insecticides and Fungicides.

In general the work of this year has followed closely the lines of previous years. Replying to a circular letter sent out last winter, thirty chemists expressed themselves as having a special interest in the work, while over twenty volunteered to perform all or a part of the desired analyses. For various reasons, the chief of which being the early date of the association's meeting, a large number of reports have not been forthcoming. The results received in time to be included in this report are as follows: Paris green, eight analysts; London purple, five; copper carbonate, two; soda lye, one; formaldehyde, four; nicotin, three. Unfortunately, among the results received, there are discrepancies in the analysis of one sample, London purple, which are hard to explain, since the same methods during the past two years have given uniformly good results.

The methods of analysis used on the Paris green sample are given in Circular No. 10 of the Bureau of Chemistry, with the exception of those for total arsenious oxid designated as I to IV, which are given below. These were published in the twentieth report of the association[a] on the pages indicated, being modifications of the Avery-Beans method for soluble arsenious oxid. The London purple methods were used as given in Circular No. 10, with the exception that in the determination of total arsenic oxid a suggestion[b] recently made for the elimination of a portion of the coloring matter was incorporated. The copper carbonate methods, the first two of the formaldehyde methods, and the Kissling nicotin method are also given in Circular No. 10. The potassium cyanid method for formaldehyde is given in the twentieth report of the association (p. 204) and the Emery nicotin method may be found in the Journal of the American Chemical Society.[c]

Paris green.

Total arsenious oxid.

Method I.—A weighed sample of the green was boiled with sodium acetate as in the determination of soluble arsenic by his [Avery's] method, the mixture filtered through asbestos, the soluble arsenic determined in the filtrate and the residue of the asbestos dissolved in dilute hydrochloric acid and titrated according to the Avery-Beans method. (Page 196.)

Method II.—Weigh out a small quantity of the finely ground green and treat with N/2 hydrochloric acid, from 5 to 10 cc for each 0.1 gram of the green present. Boil gently. If solution is not effected add a cold saturated solution of sodium acetate, using about 3 grams for each 0.1 gram of the green, and boil until all arsenious oxid is dissolved. Now add alkaline tartrate and solid bicarbonate and after dilution titrate in the ordinary way. (Avery's modification (c), page 198.)

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[a] U. S. Dept. of Agri., Bur. of Chem. Bul. 81, pp. 196–198.
[b] Ibid, p. 199.
[c] *26*:111.

Method III.—Pulverize the sample and weigh out about 0.3 to 0.4 gram in a beaker, add 25 cc of water and, while constantly stirring, add concentrated hydrochloric acid a drop at a time until all Paris green is in solution and free arsenious oxid remains as a residue. Filter and wash the residue and determine the arsenious oxid in the filtrate according to the regular Avery-Beans method. The filter and contents are washed back into the beaker, 5 grams of sodium bicarbonate added, and the solution boiled until all arsenious oxid has dissolved. The resulting solution is cooled, slightly acidified with hydrochloric acid, and made alkaline again with sodium bicarbonate and finally titrated with iodin. (Haywood's modification (*a*), page 197.)

Method IV.—Take 0.4 gram of the finely ground green and boil with 25 cc of sodium acetate (containing 12 grams) for 10 minutes. Then add concentrated hydrochloric acid a drop at a time until solution is effected (about 10 cc of the acid will be necessary). Add concentrated sodium carbonate solution a drop at a time until a slight precipitate appears, then add a solution containing 2 to 3 grams of sodium potassium tartrate and finally sodium bicarbonate in excess. Titrate with iodin in the usual manner. (Haywood's modification (*b*), page 197.)

TABLE I.—*Paris green.*

COPPER OXID.

Analyst.	Method I. (Thiosulphate.)	Method II. (Potassium cyanid.)	Method III. (Electrolytic.)
	Per cent.	*Per cent.*	*Per cent.*
R. J. Davidson and J. B. McBryde, Blacksburg, Va	29.04	29.16	28.95
	28.90	29.21	29.07
	28.99	29.12	29.07
	28.95	29.21	29.06
	28.99	29.26	.....
B. H. Smith, Bureau of Chemistry, Department of Agriculture	29.15	29.16	29.25
	29.21	29.16	29.25

SOLUBLE ARSENIOUS OXID.

Analyst.	Avery-Beans method.	Seven-day method.	Ten-day method.
	Per cent.	*Per cent.*	*Per cent.*
R. J. Davidson and J. B. McBryde, Blacksburg, Va	5.14	6.13	6.86
	5.14	6.25	6.86
	4.93	.....	.....
	5.11	.....	.....
H. J. Warner, Bureau of Chemistry, Department of Agriculture	4.67	.....	.....
	4.71	.....	.....
R. W. Thatcher, Pullman, Wash	4.44	.....	6.85
	4.49	.....	6.30
F. F. Flanders, Pullman, Wash	4.43	.....	6.11
	4.50	.....	6.77
O. M. Shedd, Lexington, Ky	[a] 4.74	.....	.....
B. H. Smith, Bureau of Chemistry, Department of Agriculture	4.76	4.05	6.68
	4.76	4.42	6.80

[a] Mean of four determinations, boiling 5 minutes.

TOTAL ARSENIOUS OXID.

Analyst.	Method I.	Method II.	Method III.	Method IV.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
S. Avery, Lincoln, Nebr	58.50	58.57	58.56	58.48
R. J. Davidson and J. B. McBryde, Blacksburg, Va	58.46	58.50	58.25	58.90
	58.40	58.12	58.96	58.87
	58.37	58.14	58.69	58.70
	58.25	.....	58.92	58.86
H. J. Warner, Bureau of Chemistry, Department of Agriculture.	58.85	58.97	58.85	59.21
	58.97	59.09	58.97	59.15
R. W. Thatcher, Pullman, Wash	59.18	[a]59.12	59.26	58.88
	59.12	59.10	58.98	58.90
F. F. Flanders, Pullman, Wash	58.61	58.99	58.88	58.77
	58.61	58.99	58.99	58.99
F. W. Robison, Agricultural College, Mich	59.04	58.49	58.79	58.32
	58.85	58.79	58.67	58.44
	58.85	58.67	58.79	58.44
O. M. Shedd, Lexington, Ky.:				
1	[b]58.20	58.93	.....	.....
2	58.07	58.68	.....	.....
3	53.95	58.93	.....	.....
4	57.23	58.87	.....	.....
5	58.56	.....	.....	.....
6	58.44	.....	.....	.....
B. H. Smith, Bureau of Chemistry, Department of Agriculture	58.49	58.47	58.53	58.44
	58.49	58.54	58.58	58.44

[a] Boiled thirty (30) minutes.
[b] See comments of analysts.

R. J. Davidson.—For the estimation of copper in the green more accurate results were obtained by using thiosulphate and cyanid solutions of one-half the strength recommended, i. e., N/20 thio and N/10 potassium cyanid.

R. W. Thatcher.—The original Avery-Beans method gives too low results, as not all of the free arsenious oxid goes into solution in dilute hydrochloric acid. Free arsenious oxid is gradually dissolved if solution is stirred vigorously, hence the total arsenious oxid obtained from such samples as this varies with the duration of stirring the mixture before neutralizing with sodium carbonate.

I prefer Method I for total arsenious oxid to all those tried, as it is easy to handle, gives satisfactory results, and by giving free and combined arsenious oxid on the same sample avoids an extra weighing. The proportion of free arsenious oxid, as dissolved by sodium acetate solution varies with the proportion used, but if these proportions be fixed in the official method, comparable results are obtained from all samples, which is all that can be said of any method I have yet seen described.

Method II gives satisfactory results if the boiling with sodium acetate solution is continued for 20 to 30 minutes, otherwise some of the free arsenious oxid remains undissolved, and low results are obtained.

Method III is satisfactory for total arsenious oxid, but variable results for the proportion dissolved on first treatment with hydrochloric acid are obtained, depending on the duration of stirring, as in the original Avery-Beans method.

Method IV is satisfactory, but gives slightly lower results than the others. It has no advantage over Method I, and does not give a determination of free arsenious oxid as does the latter.

In determining soluble arsenious oxid both the original Avery-Beans method and the preliminary reading in Method I for total arsenious oxid, give concordant results and are easy to manipulate. The amount of soluble arsenious oxid found will always be a little higher by Method I, because of the relatively larger amounts of sodium acetate used, and the exact proportions should be stipulated if the method is adopted as official.

The method of extracting the green with water for ten days is practically valueless, in my opinion, since it gives neither a measure of the free arsenious oxid present as an adulteration, nor does it represent the probable decomposition of the green in orchard practice, where the green is exposed to both moisture and carbon dioxid, the latter being very effective in decomposing Paris green.

O. M. Shedd.—In Method I for total arsenious oxid the experiments 1 and 2 were made by digesting the Paris green with the acetate solution for 2 hours on the water bath, then boiling 10 minutes gently, over a free flame, and filtering on a gooch filter; 3 and 4 were boiled with the acetate solution exactly 5 minutes and filtered on gooches. In each one a little of the Paris green ran through the filter. Experiments 5 and 6 were made by boiling exactly 5 minutes and filtering on paper filters. None of the green ran through in these.

In Method II both hydrochloric acid and acetate were used in experiments 1 and 2, while in 3 and 4 only hydrochloric acid was used.

Discussion.

The results obtained by the four methods for total arsenious oxid agree very well, the first and fourth appearing to be preferable, and it would seem wise to adopt these two methods as optional methods of determining total arsenious oxid.

As Mr. Thatcher suggests, it would be well in Method I to use the same amount of sample as has always been used with the original Avery-Beans method—that is, 1 gram, in order to obtain results comparable with the latter method.

The former referee, in Bulletin No. 68 of the Bureau of Chemistry, points out that the ten-day extraction method is not intended to give the amount of free arsenious oxid present, nor the exact decomposition of the green in orchard practice, but rather an indication of the stability of the green, since if it will break up with water free from carbonic acid gas it will most certainly break up with carbonic acid gas present. In other words, it serves as a quali-quantitative test as to the physical condition of the green, and should be used in connection with the Avery-Beans method, which gives the approximate amount of soluble arsenious oxid present.

In the determination of copper in Paris green the three methods give, as in years past, very concordant results. In the directions as sent out (Circular 10, p. 3), a slight error occurs in Method I. The method reads: "The nitric acid solution is made alkaline with sodium carbonate, then made slightly acid with acetic acid diluted with water, and about ten times the weight of the copper in potassium iodid added." The referee has found by attempting to follow these directions too literally that considerably more than ten times the weight of the copper in potassium iodid is necessary. As an excess does no harm, it is well to be on the safe side by adding a liberal quantity.

The referee recommends the adoption of the electrolytic method as the official method, and the thiosulphate method as an optional method for the estimation of copper in Paris green.

From the results obtained by the seven-day water extraction in determining soluble arsenious oxid it would not appear best to attempt to shorten the time of standing in the ten-day extraction method.

TABLE II.—*London purple.*

Analyst.	Total arsenious oxid.	Total arsenic oxid.	Soluble arsenious oxid.		Soluble arsenic oxid.	
			7-day.	10-day.	7-day.	10-day.
	Per cent.	*Per cent.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
R. J. Davidson, Blacksburg, Va.	17.35	24.26	12.26	12.50	2.14	1.99
	17.94	24.09	12.26	12.50	2.28	1.80
	.....	.....	12.13	12.01	.....	.....
R. W. Thatcher, Pullman, Wash.	9.40	32.31	12.35	12.40	2.29	4.27
	9.41	32.68	12.40	.....	1.87	.....
F. F. Flanders, Pullman, Wash.	9.70	29.45	.....	12.40	.....	4.20
	9.83	30.00	.....	.....	.....	.....
H. J. Warner, Bureau of Chemistry, Department of Agriculture	19.17	20.46	12.40	12.58	2.99	2.82
	19.09	20.40	12.58	12.74	2.86	2.88
B. H. Smith, Bureau of Chemistry, Department of Agriculture	18.09	23.63	12.40	12.41	2.21	2.07
	18.02	23.55	12.29	12.53	2.35	2.07

Comment.

R. W. Thatcher.—The methods of analysis of London purple are quite satisfactory since modified to precipitate a part of the coloring matter by sodium carbonate before making the reduction for the determination of arsenic oxid.

Discussion.

The results on London purple are very divergent and unsatisfactory, especially when we consider the excellent agreement of results which the same methods have given for the past two years.

It is difficult to assign a reason for the discrepancies of this year, and had there been time to inform the analysts of the disagreement in results, so that some work could have been repeated, it is very probable that more concordant results could have been reported.

The results on soluble arsenious oxid, however, agree very well, and show that in the case of soluble arsenious oxid in London purple a seven-day extraction gives practically the same results as the ten-day extraction, thus shortening the method appreciably.

The modification suggested by Mr. Davidson last year, for removing a portion of the coloring matter, works very well, as has been intimated, greatly facilitating the end point readings.

It has been suggested, and supported by experimental data, that a part of the arsenious oxid is oxidized to arsenic oxid by continued heating with hydrochloric acid. Acting upon this suggestion, the referee took several portions of a sample of London purple and varied the time of heating with hydrochloric acid from 5 minutes to 1 hour, but obtained practically uniform results throughout.

It will be necessary to repeat a large part of the work on London purple next year.

COPPER CARBONATE.

TABLE III.—*Copper oxid in copper carbonate.*

Analyst.	Method I (thiosulphate).	Method II (potassium cyanid).	Method III (electrolytic).
	Per cent.	*Per cent.*	*Per cent.*
R. J. Davidson, Blacksburg, Va	65.60	65.51	65.57
	65.72	65.48	65.36
	65.72	65.65	65.78
	65.80	65.36	65.68
	65.40	65.36	.....
	65.97	.....	.....
B. H. Smith, Bureau of Chemistry, Department of Agriculture	66.17	65.83	66.06
	65.77	66.10	66.12

Comments by analysts.

R. J. Davidson.—The use of half-strength solutions for titrating copper was found to give more satisfactory results. N/20 thiosulphate and N/10 potassium cyanid were used.

R. W. Thatcher.—Had no opportunity to do the copper work, but have repeatedly checked up the three methods, as described, against each other on other samples of copper compounds, and always found them to be in practical agreement.

Discussion.

The results on copper carbonate are not quite as close as have been obtained in previous trials, but, as the last comment indicates, the methods have always been in practical accord, and warrant the suggestion made under Paris green, that the electrolytic be adopted as the official method, and the thiosulphate method as an optional method.

FORMALDEHYDE.

TABLE IV.—*Formaldehyde.*

Analyst.	Solution I.		Solution II. Romijn method (potassium cyanid).
	Legler method (ammonia).	Blank and Finkenbeiner method (hydrogen peroxid).	
	Per cent.	*Per cent.*	*Per cent.*
R. Corr, Lincoln, Nebr	27.68	27.08	2.15
	27.86	27.29	2.20
	.....	.....	2.14
R. W. Thatcher, Pullman, Wash	27.89	[a]27.64	2.24
	27.77	27.66	2.22
H. J. Warner, Bureau of Chemistry, Department of Agriculture	.....	27.62	.....
	.....	27.62	.....
B. H. Smith, Bureau of Chemistry, Department of Agriculture	27.62	27.55	2.22
	27.73	27.63	2.22

[a] Let stand 15 minutes before titration.

Comment.

R. W. Thatcher.—Low and nonconcordant results were obtained at first with the hydrogen peroxid method, when the mixture was allowed to stand only a few minutes before titration.

Discussion.

Two solutions of formaldehyde were sent out this year with instructions to use the Legler (ammonia) and the Blank and Finkenbeiner (hydrogen peroxid) methods upon the stronger one and the Romijn potassium cyanid method upon the weaker solution.

In the hands of three analysts the Blank and Finkenbeiner method gave results averaging within one-tenth of a per cent of each other, and as the method has given, for the most part, excellent results in past trials, is applicable in analyzing strong solutions without dilution, and is rapid and easy of manipulation, the referee recommends its adoption as an official method. In using this method it must be remembered that a certain amount of time is required after the addition of the hydrogen peroxid before the oxidation is complete, and, as Mr. Thatcher suggests, it may be well to extend this to 15 minutes instead of 10 as in the original method. Shaking the flask with a rotary motion at intervals after the addition of the peroxid greatly facilitates the oxidation and should not be omitted.

The potassium cyanid method also gave excellent results, the several determinations of three analysts not varying more than one-tenth of a per cent. As this method is particularly applicable to dilute solutions, it would seem well to adopt this also as an official method.

NICOTIN.

TABLE V.—*Nicotin.*

Analyst.	Kissling method.	Emery's polariscopic method.
	Per cent.	*Per cent.*
James Emery, Biochemical Division, Department of Agriculture	23.60	.....
R. J. Davidson, Blacksburg, Va.	23.07	.....
	23.07	.....
B. H. Smith, Bureau of Chemistry, Department of Agriculture	23.43	23.53
	23.53	23.73
	23.38	23.44

The work on nicotin consisted in the further trial of the Kissling method, which was recommended for adoption as the official method by the last referee, fairly concordant results being obtained. In titrating nicotin distillates the referee has preferred cochineal to phenacetolin as an indicator, giving excellent end point readings, while a recent communication from Mr. F. W. Robison states that he also uses cochineal for this purpose with good results. During the year Mr. James Emery published a polariscopic method with which the referee obtained very good results.

SODA LYE.

But one report was received upon the sample of soda lye sent out, giving no opportunity for comparing results. It will therefore be necessary to continue this work during the coming year.

II. DISINFECTANTS.

In taking up the work on disinfectants it was not deemed advisable to attempt cooperative analyses until some little introductory work had been done, such as determining from inquiries sent to public health officers and others what disinfectants are most used, what methods of analysis are employed, and a preliminary

testing of such methods by the referee, and which class of disinfectants should most profitably receive the immediate attention of the association.

The inquiries as to the disinfectant most used brought out the perhaps expected reply, formaldehyde, while chlorid of lime was considered as second in importance. A number stated that they had ceased to use proprietary compounds of all kinds. In regard to the methods used in examining disinfectants the replies were noticeably reticent.

FORMALDEHYDE.

Formaldehyde, because of its use as a fungicide and insecticide, has already received considerable attention from the association, and this year we shall recommend official methods of analysis. Judging from the results given in a recent North Dakota station bulletin, commercial formaldehyde is far from being a uniform product, and any time given to this product is profitably spent.

CHLORID OF LIME.

Three methods of analysis were employed by the referee in the determination of "available chlorin" in a sample of chlorid of lime, all of which gave fairly concordant results. When bleaching powder or chlorid of lime is allowed to stand for any length of time the percentage of calcium chlorid present gradually increases at the expense of the calcium hypochlorite. For this reason, as well as because of original differences in composition, the commercial article is not of uniform quality.

In a sample examined by the referee the methods used were Penot's method, depending upon the conversion of an arsenite into an arsenate; Otto's method, where a ferrous salt is converted into a ferric salt; and a method recently proposed by J. Pontius[a] depending upon the oxidation of iodids to iodates by means of hypochlorous acid, and the liberation of iodin from iodids by means of iodates. The last method is very easily carried out and appears to give excellent results. It would doubtless be well to compare these methods, and others that may be suggested during the coming year, on a more extensive scale.

CRUDE PHENOLIC DISINFECTANTS.

Several samples of crude phenolic disinfectants have been examined by the referee. In compounds in which the hydrocarbons are held in emulsion by resin soaps considerable difficulty was found in attempting to apply the method of analysis given by Allen,[b] which is as follows:

Treat 50 grams of the sample with dilute sulphuric acid (1:3) until the liquid is distinctly acid to litmus, shake with ether, and separate—

Acid liquid.—Render alkaline with caustic soda and distill. Titrate distillate with seminormal acid, using methylorange as an indicator (1 cc normal acid neutralizes 0.079 gram pyridine).

Ethereal layer.—Shake with 20 cc (more or less according to the amount of phenols, etc., supposed to be present) of a 25 per cent solution of caustic soda and separate.

Ethereal layer.—Distil off ether and weigh residue of hydrocarbons (e. g., rosin oil, tar oil, naphthalene, etc.).

Alkaline liquid.—Acidify with sulphuric acid (1:3) and distil until no more oily drops pass over.

Distillate.—Evaporate to low bulk with 20 cc of a 25 per cent solution of caustic soda (or sufficient to fix all the phenols), transfer to a burette, acidify slightly with sulphuric acid (1:3), keeping thoroughly cool all the time, and measure layer of phenols. The volume in cubic centimeters multiplied by 1.05 equals the weight of phenols in sample taken.

Residue in retort.—Shake with ether, separate, distil off ether, and weigh residue of fatty and resin acids.

[a] Chem. Zgt., *28:* 59.

[b] Commercial Organic Analysis, 3d ed, pt. 2, *2:* 262.

With some compounds it was impossible by following this method strictly to get a satisfactory separation upon the addition of acid and ether. After some experimenting it was found that a good separation could be obtained by taking a 25 or 50 gram sample and treating with an equal amount of water in an Erlenmeyer flask; then adding an amount of concentrated acid equal in cubic centimeters to the number of grams of the compound used, adding the acid slowly and cooling under a stream of water. Finally transfer to a separatory funnel by means of ether, shake and separate.

On treating the ethereal layer with caustic soda in compounds containing resin, three distinct layers, instead of two, are apt to be formed, causing more or less confusion. In such a case the upper layer alone contains the hydrocarbons. Care must be taken not to continue the evaporation indefinitely after driving off the ether, as the hydrocarbons constantly lose in weight; the length of time of evaporating must be uniform in all cases.

In the distillation of the phenols it is essential that the distillation be continued until little liquid is left in the retort, otherwise a considerable portion of the phenols will be left with the residue of fatty and resin acids.

Recommendations.

I would respectfully recommend—

(1) That Methods I and IV of the four modifications of the Avery-Beans method of determining total arsenic in Paris green be adopted as optional official methods.

(2) That in titration of arsenic N/20 instead of N/10 iodin be used, as Mr. Davidson suggests.

(3) That the electrolytic method be adopted as the official method of determining copper in Paris green and copper carbonate, and that the thiosulphate method be adopted as an optional method, using N/20 instead of N/10 thiosulphate solution.

(4) That the work on London purple be continued.

(5) That the volumetric silver-nitrate method be adopted as the official method of determining cyanogen in potassium cyanid, and that N/20 instead of N/10 solution of silver nitrate be used.

(6) That the methods of examination of soda lye be further tested.

(7) That the Kissling method of determining nicotin be adopted as the official method, and that Mr. Emery's polariscopic method be further tested.

(8) That the hydrogen peroxid method, suggested by Avery for determining sulphur in sulphur dips and similar compounds, be adopted as a provisional method and tested by the association next year.

(9) That the Blank and Finkenbiener peroxid method be adopted as the official method of determining formaldehyde in strong solutions, and that the Romjin's potassium cyanid method be adopted as an official method for analyzing dilute solutions.

(10) That methods of examining chlorid of lime be compared.

(11) That attention be given to the analysis of phenolic disinfectants.

The following paper was submitted by the associate referee on insecticides, for publication in this connection:

THE DETERMINATION OF LIME AND SULPHUR IN SOLUTIONS OF SULPHIDS OR POLYSULPHIDS USED AS INSECTICIDES.

By S. Avery.

A number of firms are now placing sulphur dips on the market. They are used in large quantities on western ranches, hence the sulphur content is often a matter of interest. Nearly all the dips consist of a strong solution of calcium polysulphid; on exposure to the air the odor of hydrogen sulphid is noticeable and sulphur sepa-

rates out. The purchaser usually wishes to know how much dissolved sulphur a barrel of 50 gallons represents, and after some little trouble the following method has been devised. The writer is aware that no new principles[a] are involved, but hopes that his fellow workers may find the method convenient and accurate.

(1) Preparation of Reagents.

(a) Caustic soda solution. One hundred grams of sodium hydroxid in 100 cc of distilled water.

(b) Barium chlorid solution. The crytallized salt dissolved in approximately 10 times its weight of distilled water.

(c) Ammonium oxalate solution. Saturated.

(d) Hydrogen peroxid solution. An approximate 3 per cent solution of "medicinal" hydrogen peroxid, which should be free from lime and sulphates.

If the peroxid contains lime add ammonia and ammonium oxalate solutions. Decant through a filter and use the clear solution for lime determinations only. If the peroxid contains sulphates, add freshly precipitated barium carbonate and shake occasionally for several hours. Filter and use the clear solution for sulphur only.

(2) Preparation of the Sample.

Filter through a folded filter a sufficient quantity of the sample. At once deliver 10 cc to a 100 cc measuring flask and fill to the mark. Take 10 cc of the dilute solution for the determination of lime and 10 cc for the determination of sulphur.

(3) Determination of Lime.

To the measured portion of the dilute solution (2), add at once 2 cc of caustic soda and 50 cc of hydrogen peroxid. Heat on the water bath for two hours and then slightly acidify with hydrochloric acid. Now add ammonia in slight excess and filter if a precipitate appears. Determine the lime in the filtrate by precipitating with ammonium oxalate and converting into the oxid or sulphate for weighing. The weight in grams of calcium oxid, multiplied by 417.34, represents the pounds of lime in solution per barrel of 50 gallons, provided the amount taken for analysis represents 1 cc of the original sample.

(4) Determination of Sulphur.

Treat 10 cc of the dilute solution (2) with sodium hydrate and hydrogen peroxid and heat exactly as in (3). Acidify with hydrochloric acid, ignoring any cloudiness that may remain on acidifying. Precipitate with barium chlorid and determine with the usual precautions the weight of the barium sulphate formed. If the amount taken for analysis represents 1 cc of the original solution, the weight in grams of the barium sulphate found, multiplied by 57.2874, will give the pounds of sulphur per barrel of 50 gallons.

To test the accuracy of the method 0.2053 gram of roll sulphur was dissolved in sodium hydrate and treated as above. It was found that 1.4957 grams of barium sulphate equals 0.20537 gram of sulphur; 1.1591 grams of crystallized sodium thiosulphate gave 2.1649 grams of barium sulphate, equal to 0.2972 gram of sulphur—calculated 0.2993 grams sulphur. The thiosulphate was found to be not quite pure on titrating with standard iodin. From 0.2302 gram of commercial flowers of sulphur 1.6776 grams of barium sulphate, equal to 0.2303 gram of sulphur, were obtained.

The method can be used in the analysis of almost any inorganic sulphur compounds whose sulphur passes into solution on boiling with caustic alkali.

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[a] J. Petersen, Zts. anal. Chem., *42*: 406.

A discussion of the use and adulteration of disinfectants took place after the reading of Mr. Smith's report, in the course of which the following remarks were made:

Mr. Kebler. In Kansas City I was informed that large quantities of formalin, shipped into the western section of the country for the purpose of treating smut in corn, are found to be of a very inferior character. Unless there is a certain percentage of formalin present the results are not satisfactory. Bleaching powders are also very variable in quality, varying from no available chlorin at all up to 37 per cent. The standard in the United States Pharmacopœia is 35 per cent of available chlorin, and in my opinion this is a little too high. Some standard, however, should be established.

Mr. Wiley. Both scientific and public interest in the subject of disinfectants is growing rapidly. It is interesting to know that already the proprietary articles of this kind are being refused. The use of any disinfectant whose name is not branded on the label should be discouraged. The use of sulphurous acid in destroying seed smut on seed oats and seed corn so improved the appearance of the grain that the proprietors of elevators now avail themselves of this process to bring their products up in grade. By this means the lowest grade, No. 3, may be sold for the highest, or No. 1 grain. The use of sulphurous acid for such purposes is frequently legalized. The German imperial board of health has ruled that desiccated fruits containing 0.125 per cent of sulphur dioxid may be admitted into the Empire. Barrels or casks in which white wine is to be kept are commonly treated with sulphurous acid. Limits should be established beyond which the presence of sulphurous acid in wines should not go. We have adopted the maximum limit of 200 milligrams per liter, the French standard, in the inspection of imported wines.

Mr. Bigelow. A law was passed in Illinois in 1877 to the effect that "no person shall subject or cause to be subjected any barley, wheat, or other grain to fumigation by sulphur or other material, or to any chemical or coloring process whereby the color, quality, or germ of such grain is affected." This law was finally repealed, however. In Wisconsin in 1898 a similar law was passed forbidding the fumigating of grains for commercial purposes.

Mr. Thatcher. In the State of Washington it is absolutely necessary to treat the seed wheat every year, and a larger quantity of copper sulphate is used than of any other disinfectant on the market. The use of formalin is being introduced, but I have not yet found a sample that contains 40 per cent of formaldehyde. Serious complications have arisen from these conditions, and an investigation into the use of copper sulphate is proposed.

At the close of the discussion Mr. Hopkins made a motion that the report on soils be made a special order for 11 o'clock Tuesday, which motion was carried. The meeting then adjourned until 2 o'clock p. m.

MONDAY—AFTERNOON SESSION.

The afternoon session opened with the reading of the report on potash.

REPORT ON POTASH.

By F. B. Carpenter, *Referee.*

The work on potash has been confined to a study of the sodium hydrate method proposed last year, and a continuation of the investigation of methods for the determination of moisture in potash salts.

In the early part of April the usual circular letter was sent out inviting the cooperation of chemists likely to be interested in the work, and a favorable response was received from thirty-five. To these were sent three carefully prepared samples, accompanied by the following instructions:

The samples prepared for the A. O. A. C. potash work, 1904, are numbered and described as follows:

1. Acid phosphate and potash.
2. Ammoniated fertilizer.
3. Commercial kainit.

DIRECTIONS FOR THE WORK.

1. Thoroughly mix samples for analysis before beginning the work.
2. Potash in samples Nos. 1 and 2.

(a) Determine by official Lindo-Gladding method for fertilizer, described on pages 21 and 22, Bulletin 46, revised edition, U. S. Department of Agriculture, Bureau of Chemistry.

(b) Determine potash as follows: Boil 10 grams of the sample 30 minutes with 300 cc of water plus 5 cc of concentrated hydrochloric acid. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Precipitate the lime with ammonium oxalate and complete the determination in the same manner as by the Lindo-Gladding method described under (a). Ten cc of platinum solution, of such a strength that one cubic centimeter precipitates 1 per cent, is more than enough to precipitate the potash present. It is not necessary to add platinum solution enough to precipitate the soda. (This modification is proposed for trial with the view of eliminating the error due to the occlusion of potash usually experienced with the official method.)

3. Moisture in sample No. 3:

(a) Heat 2 grams, weighed on a watch glass, in an air bath for five hours at 130° C. Cool in desiccator and weigh. Repeat until weight is about constant. Report percentage of moisture after each weighing. When drying place the watch glass on a sheet of asbestos board against which the bulb of the thermometer rests.

(b) Same as (a), except with a temperature of 120° C.

(c) Heat 2 grams, weighed on a watch glass, in a steam bath at 100° C (use water bath if not convenient to use steam bath) for five hours. Cool in desiccator and weigh. Repeat until weight is constant. Report percentage after each weighing.

(d) Heat 2 grams (weighed on a watch glass) in an oil oven at 120° C for five hours. Cool in desiccator and weigh. Repeat until weight is constant. Report percentage after each weighing.

4. Make blank determinations on all reagents, using amounts required in regular analysis.

5. Use gooch crucibles for filtering the potassium platinic chlorid, dissolving with hot water after weighing the precipitate, and reweigh the crucibles.

6. Calculate potash by using the factor 0.1939. In reporting results please describe fully any modifications of methods proposed.

The date of the next meeting of the association has not yet been announced. It is probable, however, that it will be held at an earlier date than usual, and I would thank you to send in your report promptly, or at least three weeks before the meeting.

F. B. Carpenter, *Referee.*
G. S. Fraps, *Associate Referee.*

The samples were made up as follows:

	Potash (K_2O) per cent.
Sample No. 1:	
Acid phosphate (23.325 pounds)	0.11
C. P. potassium chlorid (1.675 pounds)	62.80
Total (25 pounds)	4.31
Sample No. 2:	
Acid phosphate (17.095 pounds)	.11
Animal tankage (6.25 pounds)	.27
C. P. potassium chlorid (1.655 pounds)	62.80
Total (25 pounds)	4.30
Sample No. 3:	
Commercial kainit.	

The materials used in the above mixtures were carefully analyzed for potash by the associate referee and in the laboratory of the Virginia-Carolina Chemical Company, using the official method on the C. P. potassium chlorid and both official and modified methods on the other materials. The differences in potash content on the tankage and acid phosphate by the two methods were only slight, and the results obtained by the modified method being considered more accurate, they were used in calculating the theoretical percentages in this report.

Results on the determination of potash in the samples sent out have been received from seventeen analysts, representing twelve laboratories. These results are given in Table I.

TABLE I.—*Potash determinations on samples Nos. 1 and 2.*

Analyst.	Sample No. 1.[a]				Sample No. 2.[b]			
	Official method.	Difference from theory.	Modified method.	Difference from theory.	Official method.	Difference from theory.	Modified method.	Difference from theory.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
F. P. Veitch, U. S. Department of Agriculture	4.01	.....	4.19	.....	4.05	.....	4.33	.....
	3.96	−0.32	4.21	−0.11	4.07	−0.24	4.43	+0.08
G. S. Fraps, Texas station	3.85	.....	4.24	.....	3.96	.....	4.08	.....
	3.79	− .49	4.17	− .08	3.96	− .30	4.08	− .22
	.....	.....	4.27	.....	4.08	.....	4.17	.....
M. G. Donk, Florida Agr. Dept	3.80	.....	4.19	.....	4.00	.....	4.53	.....
	3.82	− .56	4.24	− .15	4.11	− .25	4.37	+ .16
	3.64	.....	4.16	.....	4.07	.....	4.50	.....
O. M. Shedd, Kentucky station	3.81	.....	3.98	.....	4.00	.....	4.38	.....
	3.66	− .57	4.12	− .26	3.85	− .37	4.29	+ .04
J. B. Robb, Maryland station	3.76	.....	4.30	.....	4.19	.....	4.56	.....
	3.70	− .58	4.22	− .05	4.13	− .14	4.48	+ .22
H. D. Haskins, Massachusetts station	3.92	.....	4.28	.....	4.02	.....	4.18	.....
	3.88	− .41	4.24	− .05	3.98	− .30	4.16	− .13
J. W. Kellogg, Rhode Island station	4.00	.....	4.29	.....	4.03	.....	4.26	.....
	3.99	− .31	4.29	− .02	4.13	− .22	4.29	− .02
Max D. Slimmer, Chicago, Ill	3.78	.....	4.21	.....	3.98	.....	4.60	.....
	3.82	− .51	4.32	− .04	3.96	− .33	4.48	+ .24
	3.76	.....	.....	.....	.....	.....	.....	.....
S. W. Wiley, Amer. A. C. Co., Baltimore, Md	3.86	− .45	4.27	− .04	4.07	− .23	4.19	− .11
R. B. Arnold, Kentucky Tobacco-Product Company, Louisville, Ky.	3.81	.....	4.30	.....	4.09	.....	4.45	.....
	3.88	− .45	4.32	.00	.....	− .21	4.50	+ .18
	3.88	.....	.....	.....	.....	.....	.....	.....

[a] Calculated percentage, 4.31. [b] Calculated percentage, 4.30.

TABLE I.—*Potash determinations on samples Nos. 1 and 2*—Continued.

Analyst.	Sample No. 1.				Sample No. 2.			
	Official method.	Difference from theory.	Modified method.	Difference from theory.	Official method.	Difference from theory.	Modified method.	Difference from theory.
American Cotton Oil Company, Chicago, Ill.:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Feind	4.15	−0.16	4.24	−0.07	4.18	−0.12	4.37	+0.07
Tinney	3.80	− .51	4.07	− .24	3.98	− .32	4.25	− .05
Taylor	3.97	− .34	4.18	− .13	3.91	− .39	4.19	.11
A. Lowenstein, Nelson Morris & Co., Chicago	4.07	− .24	4.25	− .06	4.24	− .06	4.58	+ .28
Virginia-Carolina Chemical Company, Richmond:								
Ryland	3.90		4.20		4.00		4.26	
	3.97		4.24		4.03		4.31	
	3.98	− .36	4.35	− .05	3.93	− .31	4.19	− .05
McCance	4.03		4.27		4.17		4.25	
	4.04	− .27	4.34	− .00	4.25	− .09	4.26	− .04
Cooke	4.08		4.30		3.90		4.36	
	3.92	− .31	4.25	− .03	4.12	− .29	4.20	− .02
Carpenter	4.05		4.28		4.15		4.27	
	4.07	− .25	4.21	− .06	4.15	− .15	4.35	+ .03
M. H. Pingree, Pennsylvania station[a]	3.83		4.46		4.09		4.17	
	3.79	− .50	4.41	+ .13	3.99	− .26	4.27	− .08
Average	3.90	− .41	4.23	− .08	4.05	− .25	4.33	+ .03

[a] Received too late to be included in average or comment.

Results on moisture determined in sample No. 3 were received from eleven analysts, representing nine laboratories. The results are shown in Table II.

TABLE II.—*Moisture determined in sample No. 3.*

Analyst.	Time of drying.	Air bath at 130° C.	Air bath at 120° C.	Steam bath.	Water bath.	Oil bath at 120° C.	Air bath at 140–150° C.	Air bath at 150–160° C.
	Hours.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
F. P. Veitch, U. S. Department of Agriculture.	5	4.05			0.70			
		3.88			.75			
	17	5.20						
		5.40						
	30	5.77						
		5.92						
	36				1.05			
					1.00			
	60				1.35			
					1.25			
	16						5.80	
							5.30	
	10							10.22
								10.48
G. S. Fraps, Texas station.	5	4.32			.54			
		4.46			.58			
	7	5.01			.63			
					.64			
	9	4.87			.67			
					.70			

TABLE II.—*Moisture determined in sample No. 3*—Continued.

Analyst.	Time of drying.	Air bath at 130° C.	Air bath at 120° C.	Steam bath.	Water bath.	Oil bath at 120° C.	Air bath at 140–150° C.	Air bath at 150–160° C.
	Hours.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
O. M. Shedd, Kentucky station.	5				0.59	3.54		
					.66	3.25		
	6				.60	3.57		
					.68	3.45		
	7				.63	3.24		
					.70	3.21		
J. Bernard Robb, Maryland station.	5	4.40	3.94		.67			
		4.17	3.81		.62			
	5	3.98						
		4.07						
	6	4.57	4.19		.67			
		4.31	4.03		.67			
		4.25						
		4.26						
	7	4.62			.70			
		4.41						
		4.35						
		4.33						
	7½		4.42					
			4.61					
	10		4.45					
			4.64					
H. D. Haskins, Massachusetts station.	5	3.35			.53			
	10	3.85						
Max D. Slimmer, Chicago, Ill.	3	3.69	4.25	3.13				
		3.84	4.28	2.52				
	7	4.74	4.43	3.31				
		4.67	4.50	3.14				
	9	4.74	4.43					
		4.67	4.50					
Southern Cotton Oil Company, Chicago:								
Feind		4.87	4.27	2.10				
Tinney		3.77	3.77	2.39				
S. H. Sheib, Virginia-Carolina Chemical Company, Richmond, Va.	5	4.20				3.65		
		4.06				3.55		
		3.90						
	13					3.84		
						3.79		
	21					3.97		
						3.86		
H. M. McCance	5				.85			
					.87			
M. H. Pingree, Pennsylvania station.	5				.56			
	6				.55			
	5		3.34					
	10		4.09					
	11		4.02					
	5	5.32						
	9	5.40						

COMMENTS BY ANALYSTS.

F. P. Veitch.—I am not satisfied with any of the methods for determining moisture in potash salts. It would seem that to meet this condition we shall have to adopt some arbitrary procedure in which the conditions are minutely defined.

G. S. Fraps.—Potash: Each determination was made on a separate solution. No difficulty was experienced in washing out sodium salts. The washing with ammonium chlorid was performed by decantation. Washing out the potassium platinic chlorid made a difference of about 0.03 per cent from direct weighing.

Moisture: Impossible to keep temperature of air bath at 130°; so I do not guarantee results. The water given off at 100° is probably the hygroscopic water, and that at 130° is the water of crystallization. There is also some decomposition at the latter temperature. The determination of water of crystallization is of questionable desirability, as far as fertilizer analyses are concerned, and I am inclined to think that the temperature of 100° should be taken, as for other materials. It might also be desirable to give two methods, one for hygroscopic moisture and one for total water, including water of crystallization. After drying the samples of kainit, they were dissolved and titrated with a normal solution of hydrochloric acid, using methyl orange as indicator, with the following results:

	Chlorin lost, per cent.
Dried 9 hours at 100°	0.00 .02
Dried 5 hours at 130°	.26
Dried 9 hours at 130°	.39

As might be expected, decomposition takes place at an elevated temperature.

M. G. Donk.—The higher potash results by the modified method I attribute, not to the sodium replacing occluded potash in the precipitate of calcium phosphate, but to the fact that when the neutralization is effected with soda instead of ammonia no loss is occasioned during the ignition, which loss it is not possible to avoid during the volatilizing of ammonium sulphate as ordinarily carried out. Two determinations on No. 1, made by solution with aid of acid and precipitation with ammonia and ammonium oxalate as usual, gave 4.18 and 4.30 per cent potash when loss during incineration was avoided by covering the evaporated residue with coarse, acid-digested sand.

J. W. Kellogg.—A blank of 1 milligram was obtained in the case of the modified method and of 1.2 milligrams in the case of the official method. These blanks have been deducted in obtaining the above percentages.

In a few instances the potassium platinic chlorid was dissolved in hot water, and the gooch filter again weighed, without any material difference in the weight. In two instances in the case of the modified method the dissolved potassium platinic chlorid was evaporated to dryness with a little additional platinic chlorid and again weighed. The results were in no case less than those obtained by the first weighing, indicating that sodium in any form was not included in the potassium platinic chlorid, as it was thought might be the case with the modified method on account of the large amount of sodium present. One-third to one-fourth more platinic chlorid was added to one of the parallels than to the other, but the results do not indicate that this additional amount had any influence.

Some difficulty was experienced in dissolving the sodium platinic chlorid with the 80 per cent alcohol in the presence of the large amount of the sodium salt, which is easily removed, however, with the ammonium chlorid wash.

R. B. Arnold.—A supplemental report is made on a comparative determination of potash on ground tobacco stems, using the official and modified methods, with the

exception that the stems were boiled with water in the first instance and with water plus 5 cc of hydrochloric acid in the second, instead of incinerating, as directed by official method. The amounts of potash determined were as follows: Official method—9.73 and 9.75 per cent; modified method—10.11 and 10.05 per cent.

S. H. Sheib.—It was found impossible to maintain the temperature of the air bath at exactly 130°, even with the use of a delicate thermostat, hence the air bath was finally discarded in favor of the oil oven, which operated successfully. The samples lost weight rapidly at first, then gradually, so long as the heating was continued, and constant weight could not be obtained, even at the expiration of 20 hours.

When dried at 130° for 10 hours, the results were fairly uniform, regardless of the quantity of moisture in the sample. In several instances as much as 0.6 gram of water was added to 2 grams of the sample. On drying for 10 hours at 130° the results were reasonably in accord with those obtained by drying the sample in its original condition, under similar conditions of time and temperature.

Comments by Referee.

By referring to Table I it will be noticed that all the results by the official method are considerably under theory, while those by the modified method, with a few exceptions, come very much nearer to the calculated percentage. From the experience of the writer with the ordinary purified sodium hydrate, it would appear that some of the variations in the results by the modified method are due to the presence of potash in this reagent. As all the analysts did not accompany their report with complete data, it is not known whether or not blank determinations were made in every case. The modified method may require slightly more care in washing the potassium platinic chlorid precipitate, but, on the other hand, it requires less care in the ignition with sulphuric acid, as there is much less danger of mechanical loss accompanying the volatilization of the ammonia salts and organic matter. The question has been raised as to whether the hydrochloric acid used would not liberate some of the insoluble forms of potash. This could hardly result to any appreciable extent, as the material is only in contact with the boiling solution for half an hour, and the percentage of pure hydrochloric acid present is only 0.66 per cent.

The results in Table II, giving moisture determinations on the sample of kainit, simply confirm our previous experience and show how unsatisfactory the present official method is. The practices in different laboratories with air baths, the manner of placing thermometers, etc., renders it next to impossible for different analysts to get concordant results on samples of potash salts by the official method. It would, therefore, seem desirable to adopt some arbitrary procedure in which the conditions are definitely outlined.

Table III gives a comparison of the results on 116 samples of mixed fertilizers tested in the laboratory of the Virginia-Carolina Chemical Company by both the official and proposed methods. These analyses were made along with the regular routine work, and include all the results obtained just as they were reported. The analysts report no difficulty in manipulation, and the results show an increase in potash by the proposed method of about the amount which would be expected from our experience with the analyses of mixtures of known compositions, the average in this case being 0.20 per cent for the whole number. It will be noted that as a rule the greatest differences are obtained on samples containing a high percentage of potash.

TABLE III.—*Comparison of results on potash by official method and method proposed to the Association of Official Agricultural Chemists by the referee (Virginia-Carolina Chemical Company).*

Official method.	Proposed method.	Official method.	Proposed method.	Official method.	Proposed method.	Official method.	Proposed method.	Official method.	Proposed method.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
0.71	0.88	2.49	2.68	2.33	2.42	1.43	1.79	4.43	4.66
2.59	2.75	3.07	3.30	4.96	5.24	.99	1.35	3.38	3.59
3.67	3.73	1.69	1.80	5.36	5.58	3.47	3.78	1.99	2.30
2.03	2.15	.43	.58	1.74	1.99	1.74	2.10	1.46	1.56
1.73	2.03	3.95	4.03	3.50	3.49	3.26	3.44	1.69	2.02
2.18	2.38	2.82	2.88	1.62	1.65	8.16	8.78	3.58	4.03
1.74	2.01	1.75	1.79	4.60	4.65	3.69	3.79	3.42	3.56
.65	.59	2.12	2.22	1.18	1.21	2.39	2.56	4.08	4.32
1.81	2.09	6.57	6.86	4.00	4.17	1.46	1.86	2.51	2.66
1.59	1.70	2.64	2.75	3.71	3.94	1.56	1.74	.97	1.13
5.37	5.76	1.49	1.68	2.11	2.35	2.66	2.93	3.14	3.19
1.71	1.98	4.58	4.91	4.52	4.76	3.59	3.77	4.20	4.38
1.81	2.17	.60	.60	3.62	3.79	4.18	4.41	1.65	1.80
2.32	2.33	1.43	1.83	4.41	4.86	2.61	2.64	2.68	2.94
1.55	1.71	1.33	1.49	6.50	7.07	3.00	3.07	3.10	3.27
.82	.91	1.28	1.42	2.02	2.32	2.49	2.65	.80	.97
1.36	1.45	2.46	2.78	2.35	2.49	1.40	1.59	2.16	2.21
2.45	2.74	2.07	2.23	2.33	2.66	1.58	1.63	3.82	3.94
1.77	1.87	3.11	3.40	2.41	2.65	2.73	3.18	3.58	3.87
1.46	1.74	3.72	3.66	1.25	1.57	3.20	3.37	2.58	2.92
1.11	1.30	1.69	1.90	1.56	1.65	1.18	1.50	2.09	2.57
1.75	2.01	3.13	3.30	3.39	3.68	3.13	3.43	[a] 2.63	[a] 2.83
2.87	3.08	1.88	2.12	3.54	3.79	3.65	3.90		
3.46	3.77	2.38	2.44	1.73	2.03	4.38	4.67		

[a] Average.

RECOMMENDATIONS.

Inasmuch as the present official method for the determination of potash in mixed fertilizers does not give credit for the full amount contained, and as the slight modification proposed last year by the reporter has been tried for two years by members of the association with favorable results, I will make the following recommendation:

(1) That the directions for making the solution in mixed fertilizers given under the determination of potash methods of analyses[a] be made to read as follows: Boil 10 grams of the sample with 300 cc of water plus 5 cc of hydrochloric acid for thirty minutes. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Add sufficient powdered ammonium oxalate to precipitate all the lime present, cool, dilute to 500 cc, mix and pass through dry filter. The method for the solution of potash salts is to remain as at present.

In order to place the matter before the association, the following recommendation is made with reference to the determination of moisture in potash salts.

(2) That the directions for the determination of moisture in potash salts, sodium nitrate, and sulphate of ammonia, given under the determination of moisture, Bulletin 46, page 11, be made to read as follows:

In potash salts, sodium nitrate, and ammonium sulphate heat 2 grams at 130° in an oil oven for ten hours. The loss in weight is considered as moisture.

[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 46, p. 21.

In the absence of the referee, Mr. Jones, an abstract of the report on nitrogen was submitted to the association by Mr. Weber. The report read in full as follows:

REPORT ON THE DETERMINATION OF NITROGEN.

By C. H. Jones, *Referee.*

The work on nitrogen for the past year comprised comparisons on nitrogen availability by the provisional neutral permanganate method and the alkaline permanganate method.

Three samples were selected. No. 1, a commercial fertilizer having organic nitrogen in readily available form; No. 2, a commercial fertilizer deriving part, at least, of its organic nitrogen from unacidulated garbage tankage; and No. 3, a low grade garbage tankage.

Each sample was finely ground and carefully mixed previous to distribution. Uniformity was checked at this laboratory by nitrogen determinations on six samples selected at random from each lot.

Nitrogen No. 1—1.47, 1.51, 1.47, 1.47, 1.49, 1.47 per cent.

Nitrogen No. 2—1.30, 1.30, 1.30, 1.33, 1.30, 1.30 per cent.

Nitrogen No. 3—2.98, 2.95, 2.98, 3.08, 3.05, 2.98 per cent.

In reply to a circular letter sent March 21, 1904, requesting cooperation in the work, thirty-one calls for samples were received. Samples and the following directions were sent June 15, 1904:

DIRECTIONS FOR NITROGEN WORK, 1904.

I am sending you by mail under separate cover three samples for use in determining the availability of organic nitrogen for the Association of Official Agricultural Chemists.

Transfer each sample to a glass-stoppered bottle.

Sample No. 1—Commercial fertilizer.

Sample No. 2—Commercial fertilizer.

Sample No. 3—Tankage.

(1) Determine total organic nitrogen in each sample by the Kjeldahl or Gunning methods.

(2) Determine available nitrogen by the neutral permanganate method.

(3) Determine available nitrogen by the alkaline permanganate method.

Neutral permanganate method.

Into a 300 cc low-form Griffin beaker weigh 2 grams of the sample, if from a mixed fertilizer; if from a concentrated material use a quantity containing approximately 0.075 gram of nitrogen. Samples containing material that has been treated with acid should be washed on a 9-cm S. S. No. 595 filter to 200 cc and transferred, filter and all, to beaker. Digest this with 125 cc of permanganate solution (16 grams of pure potassium permanganate to 1,000 cc of water) in a steam or hot water bath for 30 minutes. Have the beaker let well down into the steam or hot water and keep closed with a cover glass, stirring twice at intervals of 10 minutes with a glass rod. At the expiration of the time remove from bath, add 100 cc of cold water, and filter through a heavy 15-cm folded filter. Wash with cold water, small quantities at a time, till total filtrate amounts to 400 cc. Dry and determine nitrogen in residue by Kjeldahl method.

Alkaline permanganate method.

Weigh out an amount of sample containing 0.045 gram of nitrogen, and transfer to a 600-cc distillation flask. After connecting with condenser to which the receiver containing standard acid has been attached, digest with 100 cc of alkaline permanganate solution (16 grams of potassium permanganate and 150 grams of sodium hydrate dissolved in water and made to bulk of 1 liter) for 30 minutes below the boiling point. Then boil until the distillation is completed.

Samples 1 and 2 contain superphosphate, and a preliminary washing will be necessary with the neutral permanganate method. No washing is required with the alkaline method.

Kindly report results at your early convenience.

Yours truly, C. H. JONES, *Referee.*

RESULTS.

Reports have been received from fifteen chemists, representing eleven laboratories. The detailed results appear in the following tables:

TABLE I.—*Total nitrogen.*

Analyst.	No. 1.	No. 2.	No. 3.	Remarks.
	Per cent.	*Per cent.*	*Per.cent.*	
Department of foods and feeding, Hatch experiment station, Amherst, Mass., Messrs. Smith and Tottingham.	1.46	1.26	3.03	Digested 2½ hours, Kjeldahl, with sulphate of potash.
	1.43	1.25	3.02	
	1.44	1.24	3.04	
	1.43	1.23	3.03	
S. H. Sheib, Virginia-Carolina Chemical Co., Richmond, Va.	1.40	1.19	3.04	Kjeldahl method.
	1.40	1.20	3.04	
	1.39	1.19	3.06	
	1.40	1.24	3.00	
	1.39	1.22	3.08	
	1.40	1.22	3.02	
J. H. Gibboney, Blacksburg, Va.	1.47	1.15	2.91	
	1.47	1.22	2.98	
F. A. Urner, Geneva, N. Y.	1.45	1.26	3.03	
	1.38	1.25	3.04	
	1.47	1.35	2.99	
	1.42	1.23	.....	
	1.45	1.27	.....	
G. A. Olson, Madison, Wis.	1.37	1.21	2.93	
	1.40	1.23	2.91	
	1.43	1.24	2.93	
A. M. Muckenfuss, Fayetteville, Ark.	1.37	1.23	2.86	
	1.42	1.24	2.86	
	1.36	1.20	.....	
C. D. Howard, Morgantown, W. Va.	1.43	1.27	2.98	
F. M. Hollister, Burlington, Vt.	1.47	1.30	3.05	Kjeldahl, with sulphate of potash.
	1.49	1.33	3.08	
C. H. Jones, Burlington, Vt.	1.47	1.30	2.98	Do.
J. B. Robb, College Park, Md.	1.54	1.35	3.00	Gunning method.
	1.53	1.33	2.98	
C. E. Calm, Chicago, Ill.	1.57	1.30	3.12	Average of 3.
American Cotton Oil Company, Chicago:				
Mr. Tinney	1.54	1.27	3.00	
Mr. Feind	1.35	1.17	2.87	
Mr. Cluff	1.42	1.22	2.95	

TABLE II.—*Insoluble nitrogen—neutral permanganate method.*

Analyst.	No. 1.	No. 2.	No. 3.	Remarks.
	Per cent.	*Per cent.*	*Per cent.*	
Department of foods and feeding, Hatch experiment station, Amherst, Mass., Messrs. Smith and Tottingham.	0.15	0.11	1.06	2 grams material used with No. 3. No excess of permanganate.
	.15	.10	1.04	
	.17	.10	1.17	
	.16	.09	1.15	
S. H. Sheib, Richmond, Va.	.17	.14	1.07	
	.19	.15	1.04	
J. H. Gibboney, Blacksburg, Va.	.28	.36	1.19	
	.35	.28	1.19	
F. A. Urner, Geneva, N. Y.	.37	.30	1.19	No excess of permanganate with No. 3.
	.37	.31	1.18	
G. A. Olson, Madison, Wis.	.35	.23	1.46	
	.35	.24	1.48	
	.35	.23	.....	
A. M. Muckenfuss, Fayetteville, Ark.	.14	.12	.79	
	.12	.11	1.01	
C. D. Howard, Morgantown, W. Va.	.10	.085	1.41	No excess of permanganate with No. 3.
	.10	.085	1.42	
F. M. Hollister, Burlington, Vt.	.23	.20	1.43	Do.
	.21	.19	1.44	
C. H. Jones, Burlington, Vt	.23	.16	1.27	Do.
J. B. Robb, College Park, Md.	.21	.19	1.18	
	.18	.17	1.22	
C. E. Calm, Chicago, Ill	1.08	.79	1.48	Average of 3 determinations in each case.
American Cotton Oil Company, Chicago:				
Mr. Tinney	.20	.17	.80	No excess of permanganate with No. 3.
Mr. Feind	.09	.27	.29	
Mr. Cluff	.13	.08	.36	

TABLE III.—*Available nitrogen—alkaline permanganate method.*

Analyst.	No. 1.	No. 2.	No. 3.	Remarks.
	Per cent.	*Per cent.*	*Per cent.*	
Department of foods and feeding, Hatch experiment station, Amherst, Mass., Messrs. Smith and Tottingham.	0.83	0.50	0.63	Digested ½ hour and distilled 75 cc.
	.82	.49	.63	
	.82	.49	.65	
	.81	.48	.64	
S. H. Sheib, Richmond, Va	.94	.55	.78	
	.94	.51	.77	
	.84	.52	.71	
	.91	.51	.71	
	.90	.51	.....	
J. H. Gibboney, Blacksburg, Va	.86	.48	.72	
	.84	.47	.74	
F. A. Urner, Geneva, N. Y	.89	.71	.95	
	.89	.62	.96	
	.....	.63	.....	
G. A. Olson, Madison, Wis	.73	.48	.54	
	.75	.46	.55	
	.74	.47	.....	
A. M. Muckenfuss, Fayetteville, Ark	.91	.44	.63	
	.89	.48	.69	
	.....	.....	.74	
F. M. Hollister, Burlington, Vt	.85	.50	.67	
	.86	.50	.67	
C. H. Jones, Burlington, Vt	.86	.53	.62	
	.85	.53	.62	
J. B. Robb, College Park, Md	1.11	.64	.85	
	1.10	.....	.79	
C. E. Calm, Chicago, Ill	1.05	.96	1.20	Average of 3 determinations.
American Cotton Oil Company, Chicago:				
Mr. Tinney	.96	.81	.56	
Mr. Feind	.88	.68	.63	
Mr. Cluff	.92	.61	.56	

TABLE IV.—*Summary of nitrogen work, 1904.*

Analyst.	Total nitrogen.			No. 1.				No. 2.				No. 3.			
				Neutral.		Alkaline.		Neutral.		Alkaline.		Neutral.		Alkaline.	
	No. 1.	No. 2.	No. 3.	Insoluble nitrogen.	Availability.	"Volatile" nitrogen.	Availability.	Insoluble nitrogen.	Availability.	"Volatile" nitrogen.	Availability.	Insoluble nitrogen.	Availability.	"Volatile" nitrogen.	Availability.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
P. H. Smith, Massachusetts	1.45	1.26	3.03	0.15	89.7	0.83	57.2	0.11	91.3	0.50	39.7	[a]1.05	65.3	0.63	20.8
W. E. Tottingham, Massachusetts	1.44	1.24	3.04	.17	88.2	.82	56.9	.10	91.9	.49	39.5	[a]1.16	61.8	.65	21.4
S. H. Sheib, Virginia	1.40	1.21	3.04	.18	87.1	.91	65.0	.15	87.6	.52	43.0	1.06	65.1	.74	24.3
J. H. Gibboney, Virginia	1.47	1.19	2.95	.31	78.9	.85	57.8	.31	73.9	.48	40.3	1.19	59.7	.73	24.7
F. A. Urner, New York	1.42	1.27	3.02	.37	73.9	.89	62.7	.31	75.6	.65	51.2	1.19	60.6	.96	31.8
G. A. Olson, Wisconsin	1.40	1.23	2.92	.35	75.0	.74	52.9	.23	81.3	.47	38.2	1.47	49.7	.55	18.8
A. M. Muckenfuss, Arkansas	1.38	1.22	2.86	.13	90.6	.90	65.2	.12	90.2	.46	37.7	.90	68.5	.69	24.1
C. D. Howard, West Virginia	1.43	1.27	2.98	.10	93.0	.....	.....	.09	92.9	.....	.....	1.42	52.3	.....	.....
F. M. Hollister, Vermont	1.48	1.32	3.06	.22	85.1	.86	58.1	.20	84.8	.50	37.9	1.44	52.9	.67	21.9
C. H. Jones, Vermont	1.47	1.30	2.98	.23	84.4	.86	58.5	.16	87.7	.53	40.8	1.27	57.4	.62	20.8
J. B. Robb, Maryland	1.53	1.34	2.99	.20	86.9	1.11	72.6	.18	86.6	.64	47.8	1.20	59.9	.82	27.4
C. E. Calm, Illinois	1.57	1.30	3.12	[b]1.08	[b]31.2	1.05	66.9	[b].79	[b]39.2	[b].96	[b]73.8	1.48	52.6	1.20	38.5
Mr. Tinney, Illinois	1.54	1.27	3.00	.20	87.0	.96	62.3	.17	86.6	[b].81	[b]63.8	[b].80	[b]73.3	.56	18.7
Mr. Feind, Illinois	1.35	1.17	2.87	.09	93.3	.88	65.2	.27	76.9	.68	58.1	[b].29	[b]89.9	.63	22.0
Mr. Cluff, Illinois	1.42	1.22	2.95	.13	90.8	.92	64.8	.08	93.4	.61	50.0	[b].36	[b]87.8	.56	19.0
Average	1.45	1.25	2.99	.20	86.2	.90	62.0	.18	85.6	.54	43.2	1.26	57.9	.72	24.1

[a] Two grams material taken. Omitted from average.

[b] Omitted from average.

COMMENTS OF ANALYSTS.

Department of foods and feeding, Hatch experiment station, Amherst, Mass.—A uniform quantity of distillate was necessary with the alkaline permanganate method to obtain concordant results.

J. B. Robb, College Park, Md.—In the distillation of the alkaline method I found it necessary to distill until the contents of the flasks were brought almost to dryness, as nitrogen seemed to be given off as long as the distillation was continued. With sample No. 1 the percentage of nitrogen in the different distillates was as follows:

	Per cent nitrogen.
First distillate of 33 cc gave	0.92
Second distillate of 22 cc gave	.09
Third distillate of 21 cc gave	.07
Fourth distillate of 15 cc gave	.13

F. A. Urner, Geneva, N. Y.—With the neutral method sample No. 3 showed a complete decolorization with 200 cc permanganate solution.

A. M. Muckenfuss, Fayetteville, Ark.—In the neutral method I used a deep 400 cc ordinary beaker and washed the precipitate on a 5½ cm No. 589 S. S. cut filter. At the last filtration I used a 12½ cm ordinary cut filter, two pieces to the determination.

In the alkaline method I used a 750 cc round-bottom flask for the digestion. No blanks were made except in the determination of total nitrogen.

C. D. Howard, Morgantown, W. Va.—We use the Wesener distillation apparatus (with steam), and on this account a test of the alkaline method has been omitted, the dilution of the permanganate by condensed steam doubtless making it impossible to obtain results that would be comparable with the others.

The neutral permanganate method has been employed successfully at this station for the past two years, in connection with the fertilizer inspection. Hitherto it has been our custom to use a 2-gram charge, but in view of the fact that the majority of the complete fertilizers on sale in this section are made up with but 1 per cent of nitrogen, the advisability is being considered of employing 3 grams in the work of the coming season. I might state that the suggestion embodied in the method, viz, drying of the filter paper and contents after washing, has never been followed in this laboratory, as we have found it perfectly satisfactory to use a wide-necked flask and burn wet.

Attention should be called to the fact that in the C. S. & S. No. 588 folded filters, the content of nitrogen has been uniformly observed to be 0.00075 gram. This quantity, of course, if not taken into account, would involve a considerable error in nitrogen availability work.

In the case of sample No. 3 it would seem that the ratio of total nitrogen to organic matter is much greater than ordinarily occurs in practice.

Discussion of Results.

The results on the whole are very satisfactory. Total nitrogen determinations show extreme variations of 0.22, 0.17, and 0.26 per cent on samples 1, 2, and 3, respectively.

Results by the neutral permanganate method agree closely and indicate that if directions are adhered to in the digestion with the permanganate solution uniform results may be obtained by different operators. This method as now modified requires 2 grams of material to be used in the case of commercial fertilizers. I am of the opinion that this amount is too small and that too high an availability would be shown on low-grade fertilizers containing organic nitrogen from questionable sources.

In the case of samples 1 and 2 sent out by the referee the former has shown a high and the latter a relatively low availability, year after year, by both pepsin and alkaline permanganate methods, and we have good grounds for believing garbage tankage was used as a partial source of nitrogen in No. 2. The results reported show the average availability by the neutral method to be practically the same in each case—No. 1, 86.2 per cent; No. 2, 85.6 per cent; while seven of the fifteen analysts report the higher availability for No. 2.

Tests were run in the Vermont laboratory on samples 1 and 2 by the neutral method, using an amount of material equivalent to 0.075 gram of nitrogen. The results show an availability of 93.5 per cent for No. 1 and 83.2 per cent for No. 2. The alkaline permanganate method shows an average availability of 62, 43, and 24 per cent, respectively, and clearly indicates a difference in the quality of organic nitrogen in samples 1 and 2. Both methods clearly show the inferiority of the nitrogen in the garbage tankage.

The chief trouble found in operating the alkaline method seems to be from excessive frothing during distillation and an uncertainty as to when to stop. Provided the heat is increased gradually after the thirty minutes' digestion serious frothing will never occur. Regarding the conclusion of the process the results following are submitted.

TABLE V.—*Results on first, second, third, and fourth distillates, alkaline method.*

Sample No.	Amount of first distillate.	Nitrogen.	Second distillate.	Nitrogen.	Third distillate.	Nitrogen.	Fourth distillate.	Nitrogen.
	cc.	*Per cent.*	*cc.*	*Per cent.*	*cc.*	*Per cent.*	*cc.*	*Per cent.*
1.....	45	0.771	20	0.032	19	0.032	10	0.023
1.....	40	.726	22	.050	18	.057	10	.011
2.....	46	.477	17	.020	18	.030	14	.010
2.....	47	.480	18	.026	17	.020	8	.010

Omitting the last portion driven over it will be seen that 84, 80, 81, and 82 cc of distillate were obtained, and that they carried 97.3 per cent, 98.7 per cent, 98.1 per cent, and 98.1 per cent of the total nitrogen secured when the distillation was continued nearly to dryness.

RECOMMENDATIONS.

(1) The referee would recommend that the alkaline permanganate method, amended to read as stated below, be adopted as a provisional method.

ALKALINE PERMANGANATE METHOD.

Weigh out an amount of sample containing 0.045 gram of organic nitrogen, and transfer to a 600 cc distillation flask. After connecting with the condenser to which the receiver containing standard acid has been attached, digest with 100 cc of alkaline permanganate solution (16 grams of potassium permanganate and 150 grams of sodium hydrate, dissolved in water and made to bulk of 1 liter), for thirty minutes below the boiling point. Then boil until 85 cc of distillate is obtained. If the material shows a tendency to adhere to the sides of the flask an occasional gentle rotation is necessary during distillation.

(2) That the study of availability by both neutral and alkaline methods be continued, particularly with a view to determining the amount of material to be used in the neutral method on commercial fertilizers.

Mr. FRAPS. At a previous meeting of this association Mr. Withers and myself presented some work on the availability of nitrogen in fertilizers, in which it was found that the amounts of nitrates produced from different materials were in the same order as their availability measured by the vegetation tests of Jenkins and Britton and by permanganate of potash. Later experiments by Mr. Withers and myself, however, showed that this order was not always the same in different soils, and considerable variation was found. I have taken up this subject again at the Texas station, and have found that, while the amount of nitrates produced is liable to great variations and depends largely upon the nature of the *soil*, the amount of nitrates plus ammonia formed depends chiefly upon the nature of the *material*, and hardly at all upon the nature of the soil. The amount of nitric and ammoniacal nitrogen produced from given materials under comparable conditions is a means of comparing their availability.

The reports on the separation of nitrogenous bodies being in order the following letter from the referee in charge of the subject of milk and cheese proteids was read:

Dr. H. W. Wiley, *Washington, D. C.*

Dear Sir: As referee on the separation of nitrogenous bodies in milk and cheese, I wish to say that our work is so incomplete that it would be impossible for me to prepare a report for the September meeting of the association. The character of the work is also such that I have not asked cooperation of the other men mentioned in the list you sent me on March 10. The fundamental and research character of this work demands the special efforts of those most interested in this particular line, and only as they are taken up as supplementary to some problem do they receive the attention needed. My absorption in phosphorus metabolism study the past year has prevented my carrying to completion any work started in milk chemistry. As we expect to again resume our studies on cheese and milk, opportunity may be afforded to further carry out and test certain methods now in use.

I regret that as referee I can report no progress, but hope that those chemists most interested in this subject will have worked independently of any instructions.

Respectfully,

E. B. Hart, *Referee.*

The report of the associate referee on the separation of vegetable proteids was presented by the secretary and reads in full as follows:

REPORT ON THE SEPARATION OF VEGETABLE PROTEIDS.

By Joseph S. Chamberlain, *Associate Referee.*

The referee for last year having presented a résumé of the work that has been done on the general subject of the separation of vegetable proteids, it was considered best to confine the work of this year to the separation of the proteids of a single plant, viz, wheat.

In a paper presented at the last meeting[a] a method based upon the work of Osborne and Voorhees was described, the object of which was an accurate separation of the proteids of wheat into three groups. The first group contains those proteids soluble in dilute salt solution and includes the individual proteids, globulin, albumin, and proteose of Osborne and Voorhees. The second group consists of the single proteid gliadin and the third of the single proteid glutenin. It was shown that in the ordinary extraction of wheat with alcohol the extract contains not only the single proteid gliadin, but also a large part of those proteids which are soluble in dilute salt solution, and also, that the alcohol insoluble residue contains, with the glutenin, a small amount of the salt solution soluble proteids. Thus the alcoholic extract of wheat, when made on a sample not previously extracted with salt solution, does not contain simply gliadin, and corrections are necessary for the overlapping of the several groups of proteids. This overlapping of the different proteids in the ordinary extraction method of separation is very important, if we desire to separate into individuals the proteid constituents of wheat.

One of the collaborators for this year, Prof. H. Snyder, has carried through a series of determinations parallel to those referred to in last year's proceedings which agree with them in regard to the overlapping of the salt solution soluble proteids upon the alcohol soluble and alcohol insoluble. He also made the determinations by his polariscope method, and suggests the following correction for the globulin present in the alcoholic extract, thus making this method applicable both in determining total proteids soluble in alcohol and in correcting for overlapping:

"To remove proteids soluble in 5 per cent potassium sulphate from the alcoholic solution, polarize the alcoholic solution as directed.[b] To 50 cc of the alcoholic solu-

[a] Proceedings A. O. A. C., 1903, Bul. 81, Bureau of Chemistry, pp. 118-125.

[b] J. Am. Chem. Soc., *26:* 263.

tion add 40 cc potassium sulphate solution, evaporate to 25 cc to remove the alcohol, make up to 50 cc, and filter. Polarize and deduct from first polarization."

While the question of the overlapping of the different proteids is thus touched upon in this report, and while it was originally considered to be of the most importance, yet it was not gone into further at this time because it was considered best to first establish the fact as to whether or not the simple extraction with salt solution and alcohol would yield concordant results as to total proteid content of the extract and leave the problem of separation into individual proteids for future work.

To assist in the work of testing the uniformity of the results obtained by extracting wheat with alcohol and salt solution, the referee secured the collaboration of five other chemists, viz, J. A. Le Clerc and F. C. Weber of the Bureau of Chemistry, H. Snyder of the Minnesota station, R. Harcourt of the Ontario Agricultural College, and E. F. Ladd of the North Dakota station. Five samples of flour were sent out in rubber-stoppered bottles with the following directions:

JULY 12, 1904.

DEAR SIR: As associate referee on the separation of vegetable proteids for the A. O. A. C. for 1903–4, I am anxious to have a few determinations made to test the uniformity of results secured by different persons in the separation of the proteids of wheat by the method proposed at the A. O. A. C. meeting, 1903. Also it is desired to compare results obtained by this method for the alcohol-soluble proteids with results obtained in the determination of gliadin by the polariscope method of H. Snyder.

The material consists of five samples of flour. It is desired to have a set of duplicate determinations made on each sample.

(1) Determine moisture at 105° C in an atmosphere of hydrogen or coal gas, if possible; otherwise, at 100° C in steam oven.

(2) Determine (a) proteids soluble in salt solution, (b) proteids soluble in alcohol, and (c) proteids insoluble in alcohol by (2), (3), (4), and (5) of the proposed method. (A. O. A. C. Proceedings, 1903, Bureau of Chemistry, Bul. 81, pp. 124, 125.)

(3) If desired, instead of (4) of the proposed method, determine gliadin by the polariscope method of H. Snyder. (J. Am. Chem. Soc. *26:* 263.)

(4) Report each separate determination calculated to air dry material as received, and also any modification introduced or any suggestions for improvement of the method.

(Signed) JOSEPH S. CHAMBERLAIN, *Associate Referee.*

No attempt was made to separate the individual proteids, but simply to secure results on the three groups of proteids—those soluble in salt solution, those soluble in alcohol, and those insoluble in alcohol. The results obtained by the various workers are given in the following table:

TABLE I.—*Results of collaborative work on separation of vegetable proteids.*

PROTEIDS SOLUBLE IN 5 PER CENT POTASSIUM SULPHATE.

Serial number.	J. S. Chamberlain.		J. A. LeClerc.		E. F. Ladd, A. H. Kimberly.		H. Snyder.		F. C. Weber.		R. Harcourt, H. L. Fulmer.	
	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
202....	0.265	1.50	0.214	1.21	0.28	1.59	.....	.....	0.268	1.52	0.273	1.55
209....	.220	1.25	.258	1.46	.29	1.65	0.27	1.535	.285	1.62	.395	[a]2.24
251....	.265	1.50	.236	1.34	.266	1.51	.27	1.537	.26	1.48	.289	1.64
253....	.29	1.65	.36	2.04	.304	1.72	.29	1.66	.345	1.96	.314	1.785
254....	.285	1.62	.288	1.64	.355	2.02	.31	1.77	.323	1.83	.345	1.96

[a] Not included in the averages.

TABLE I.—*Results of collaborative work on separation of vegetable proteids*—Continued.

PROTEIDS SOLUBLE IN ALCOHOL, BY NITROGEN DETERMINATION.

Serial number.	J. S. Chamberlain.		J. A. LeClerc.		E. F. Ladd, A. H. Kimberly.		H. Snyder.		F. C. Weber.		R. Harcourt, H. L. Fulmer.	
	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.	Nitrogen.	Proteid.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
202	1.08	6.13	1.00	5.68	0.928	5.27	.....	.....	1.08	6.13	1.06	6.03
209	.79	4.49	.832	4.72	.672	3.82	0.736	4.18	.755	4.29	.732	4.16
251	1.045	5.94	.935	5.31	.952	5.407	.986	5.60	.99	5.63	.994	5.645
253	1.08	6.13	.995	5.65	1.02	5.793	1.045	5.938	1.10	6.25	.978	5.56
254	1.20	6.81	1.08	6.13	1.20	6.81	1.186	6.474	1.21	6.87	1.11	6.315

PROTEIDS SOLUBLE IN ALCOHOL, BY POLARISCOPE METHOD.

202	.....	.....	.....	.....	0.66	3.748	.....	.....	.....	.....	.....	.....
209	.....	.....	.....	.....	.33	1.875	0.74	4.20	.....	.....	.....	.....
251	.....	.....	.....	.....	.638	3.624	1.00	5.68	.....	.....	.....	.....
253	.....	.....	.....	.....	.836	4.748	1.04	5.91	.....	.....	.....	.....
254	.....	.....	.....	.....	.88	4.998	1.16	6.59	.....	.....	.....	.....

PROTEIDS INSOLUBLE IN ALCOHOL.

202	0.758	4.30	0.80	4.54	0.929	5.28	.....	.....	0.785	4.45	0.875	4.97
209	.56	3.19	.60	3.41	.616	3.50	0.575	3.27	.615	3.49	.627	3.56
251	.674	3.83	.78	4.43	.809	4.595	.657	3.73	.785	4.45	.851	[a]4.835
253	.71	4.03	.786	4.46	.75	4.26	.694	3.944	.73	4.15	.838	4.76
254	.947	5.38	1.03	5.85	.979	5.56	.958	5.44	1.05	5.96	1.03	5.825

TOTAL PROTEIDS.

202	1.82	10.34	.....	.....	1.80	10.22	.....	.....	1.86	10.56	1.83	10.395
209	1.35	7.68	.....	.....	1.25	7.10	1.295	7.36	1.33	7.55	1.335	7.585
251	1.76	9.99	.....	.....	1.725	9.79	1.708	9.704	1.77	10.05	1.75	9.925
253	1.79	10.17	.....	.....	1.805	10.25	1.709	9.707	1.81	10.28	1.805	10.25
254	2.10	11.93	.....	.....	2.12	12.04	2.037	11.57	2.10	11.93	2.14	12.15

SUM OF ALCOHOL-SOLUBLE AND ALCOHOL-INSOLUBLE PROTEIDS.

202	1.838	10.43	1.80	10.22	1.857	10.55	.....	.....	1.86	10.58	1.936	11.00
209	1.35	7.68	1.432	8.13	1.288	7.32	1.311	7.45	1.37	7.78	1.36	7.72
251	1.72	9.77	1.715	9.74	1.761	10.02	1.643	9.328	1.77	10.08	1.845	[a]10.48
253	1.79	10.15	1.78	10.11	1.77	10.05	1.739	9.88	1.83	10.40	1.82	10.32
254	2.147	12.19	2.11	11.98	2.179	12.37	2.144	12.01	2.26	12.83	2.14	12.14

[a] Not included in the averages.

TABLE II.—*Averages of results given in Table I and maximum differences.*

PROTEIDS SOLUBLE IN 5 PER CENT POTASSIUM SULPHATE.

Serial number.	Average.		Maximum difference.	
	Nitrogen.	Proteid.	Nitrogen.	Proteid.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
202	0.260	1.47	0.066	0.380
209	.265	1.503	.070	.400
251	.266	1.501	.053	.30
253	.317	1.803	.070	.390
254	.318	1.81	.070	.397
Average			.066	.375

PROTEIDS SOLUBLE IN ALCOHOL, BY NITROGEN DETERMINATION.

202	1.029	5.85	0.152	0.86
209	.753	4.27	.160	.90
251	.984	5.59	.110	.63
253	1.036	5.89	.122	.69
254	1.166	6.57	.130	.74
Average			.135	.760

PROTEIDS INSOLUBLE IN ALCOHOL.

202	0.829	4.71	0.171	0.980
209	.599	3.40	.067	.37
251	.741	4.21	.152	.865
253	.751	4.27	.144	.816
254	.998	5.67	.103	.580
Average			.127	.722

TOTAL PROTEIDS.

202	1.83	10.38	0.060	0.340
209	1.31	7.45	.150	.850
251	1.743	9.89	.068	.346
253	1.784	10.13	.096	.543
254	2.099	11.92	.103	.580
Average			.095	.532

SUM OF ALCOHOL-SOLUBLE AND ALCOHOL-INSOLUBLE PROTEIDS.

202	1.86	10.55	0.136	0.360
209	1.352	7.68	.144	.810
251	1.723	9.787	.132	.752
253	1.788	10.16	.091	.520
254	2.163	12.25	.150	.850
Average			.131	.742

Without commenting upon the results in detail the following conclusions may be drawn:

As was expected, the agreement is closer in the case of proteids soluble in salt solution than in the other two groups, the maximum difference between any two determinations being 0.07 per cent nitrogen, equivalent to 0.40 per cent of proteid.

Two of the workers, F. C. Weber and the referee, tried both 2-gram and 4-gram samples to determine the effect on the result of using the same amount of solvent and different amounts of substance. While the results are not quite in agreement, yet they show clearly that exact methods of work should be followed in regard to the amount of material and solvent and also as to time and manner of treatment. With these precautions there seems to be no doubt that uniform results will be obtained for proteids soluble in a salt solution.

With the proteids soluble in alcohol there seems to be an improvement necessary in the manipulation, defects in which it is believed cause the discrepancies. In carrying out the extraction in a Kjeldahl digestion flask, as directed, using 100 cc of alcohol, a considerable quantity of the flour persistently remains adhering to the portions of the flask above the liquid and consequently is not thoroughly extracted unless shaken continually. If a small Erlenmeyer flask is used and the residue washed completely onto the filter paper in order to transfer it to a Kjeldahl flask, it is equally difficult to remove the last traces of residue from the flask. The extraction was originally made in a Kjeldahl flask in order to avoid the necessity of removing the residue from the flask and at the same time to have it in condition for the determination of nitrogen. In all of the determinations, however, and in a much larger number that have been carried through by the referee, there is always a very close agreement, as would be expected, between the sum of the alcohol-soluble and alcohol-insoluble proteids and the total proteids found by nitrogen determination. It would seem better, therefore, to carry out the alcoholic extraction in a small flask, as in the case of the salt solution extract, thus insuring practically complete contact between the substance and the solvent. The residue from the alcoholic extraction need not be removed from the flask for nitrogen determination, but the alcohol-insoluble proteids may be determined by the difference between the total proteids and proteids soluble in alcohol. With these modifications and precautions it is believed that the method will yield satisfactory results.

Recommendations.

Until further work can be done upon the question of the overlapping of the different proteids, the referee recommends the following:

(I) That for the present no attempt be made by the following method to separate the proteids of wheat into individuals, and that only such names be applied as describe the process of separation, viz, (a) proteids soluble in alcohol; (b) proteids insoluble in alcohol; (c) proteids soluble in dilute salt solution.

(II) That the following method for the separation of the proteids of wheat be used provisionally:

(A) Total proteids:

Determine total nitrogen by the Gunning method. Nitrogen×5.68=total proteids.

(B) Proteids soluble in alcohol:

(1) Weigh out 2 grams of flour into a small flask holding only slightly more than 100 cc—about 110 cc. Add 100 cc of 70 per cent alcohol and shake thoroughly for 15 minutes. Allow to stand 18 hours and filter into a Kjeldahl digestion flask. Wash the residue with 100 cc of alcohol. Add to the total filtrate 5 to 10 cc of concentrated sulphuric acid and distill off the excess alcohol, continuing the distillation until fumes appear. Determine nitrogen by the Gunning method. Nitrogen×5.68= proteids soluble in alcohol.

(2) Determine proteids soluble in alcohol by Snyder's polariscopic method.[a]

(C) Proteids insoluble in alcohol:

Subtract proteids soluble in alcohol from total proteids to obtain proteids insoluble in alcohol.

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[a] J. Amer. Chem. Soc., *26:* 263.

(D) Proteids soluble in dilute salt solution:

Use a 5 per cent solution of potassium sulphate. Place 4 grams of the flour in a flask such as is used in (B1), and introduce exactly 100 cc of the salt solution. Shake thoroughly and allow to stand, with frequent shakings, for 18 hours, or better still, agitate in a shaker for 6 hours. After standing to settle, filter off 50 cc of the liquid, pouring back the first portions of the filtrate until it filters clear, and determine the nitrogen therein by the Gunning method. The amount found multiplied by 2 gives the nitrogen in the original flour. This result multiplied by 5.68 gives the amount of proteids in the flour soluble in a 5 per cent potassium sulphate solution.

(III) That further tests as to the overlapping of the different proteids be made.

Mr. Wiley. I would like to make an inquiry as to the factor used for calculating proteids.

Mr. Snyder. We have been using both 5.68 and 6.25, but the factor 5.68 is used only to a slight extent.

Mr. Wiley. I understand that you are in the habit of using the factor 5.68 or 5.7 and calling attention to it, and when no mention is made the use of 6.25 is understood.

In the absence of the associate referee on meat proteids this report was passed over, but is here given in full:

REPORT ON THE SEPARATION OF MEAT PROTEIDS.

By W. D. Bigelow, *Associate Referee.*

The chief work undertaken this year was a repetition of that reported in 1903 on the separation of the nitrogenous bodies in meat extracts. Owing to the unreliable results obtained by bromin, both alone and in conjunction with other reagents, it was considered best to eliminate it altogether from the work. The other precipitants employed last year were again studied, using 8 meat extracts and similar substances. In addition 30 typical meat extracts and similar products were procured and a complete examination was made of them. The report on this work is not presented here in detail but several suggestions are made, based on determinations not specifically mentioned in this report.

In the following tables are given the results obtained by precipitating solutions of meat extract by means of zinc sulphate, phosphotungstic acid, and tannin salt, respectively. The filtrates from the precipitates thus obtained are divided into aliquot parts and one part from each treated with each of the other reagents for the purpose of determining what combination gives the highest result. The figures obtained do not entirely confirm the work of last year. The following statement, however, was made in the report submitted in 1903:

These results are submitted merely as preliminary. They have not been confirmed, and have been obtained on so few samples that the reporter feels that no conclusion should be drawn from them. The discrepancies in the results of two reagents added in different order are surprising and should be confirmed before being accepted. At the same time, the general agreement among them suggests the advisability of continued study of the combinations of the various reagents employed.

As before stated, a further and more detailed study has confirmed those results only in part. The differences between the results of this year and those of last year are partially due to closer study of the tannin salt method. In this determination the amount of sodium chlorid present in the extract and the volume of the solution must be carefully considered, as the tannin salt precipitate is somewhat soluble and

its amount decreases rapidly with the increase of volume of the solution. In order to secure a uniform salt content the sodium chlorid in the ash of the meat extracts is determined, and sodium chlorid is then added to the portion of the solution employed in the determination of the tannin salt precipitate in sufficient quantity to make the total amount of sodium chlorid present 1 gram.

In the samples included in this report the amount of precipitate obtained with the tannin salt reagent in various dilutions of the different extracts is given in the following table:

TABLE I.—*Precipitate obtained with the tannin salt reagent and various dilutions of the extracts.*

Serial number.	Total nitrogen.	Dilution.		
		60 cc.	100 cc.	200 cc.
11143	9.66	4.50	3.88	2.71
11144	8.25	4.52	3.81	3.32
11145	7.57	3.64	3.04	2.52
11146	8.54	4.31	3.41	2.65
11147	4.68	1.96	1.70	1.48
11148	3.10	.56	.38	.22
11149	12.38	11.05	10.28	9.79
11150	14.20	11.10	8.45	7.08

It is thus apparent that the less the volume of the solution the higher will be the results obtained. At the same time there is, of course, a limit to the concentration that can be employed. Mr. Cook found that 60 cc was as small an amount of the solution as could be used with satisfactory results. Owing to the solubility of this precipitate it is obviously impracticable to wash it. In order to secure reliable results it is necessary to make the solution up to a definite volume, filter, and determine nitrogen in an aliquot portion of the filtrate.

There are given below results of the various precipitates and combinations of precipitates in terms of percentage of the original sample and in terms of percentage of total nitrogen. These results are so arranged as to facilitate comparison. It is apparent that of all single reagents the highest results are given by the phosphotungstic acid, except in substances which contain large amounts of peptones. The most satisfactory results are obtained from a combination of phosphotungstic acid and tannin salt, preferably in the order given. The phosphotungstic acid should first be removed by filtration, and the tannin salt precipitate thrown down in the filtrate from the phosphotungstic acid precipitate and separated by filtration. Since it is practicable to wash the precipitate obtained with phosphotungstic acid with water, the entire filtrate may be concentrated by evaporation and employed for the determination of the tannin salt precipitate. The two precipitates may then be combined, and a single determination of nitrogen will suffice.

In working with samples containing a large amount of the simpler amids Mallet's method, employing phosphotungstic acid in the heat, is preferable. In that case, however, it will be necessary to use the tannin salt reagent first or to allow the filtrate from the phosphomolybdate precipitate to cool, then filter and discard the precipitate.

TABLE II.—*Separation of proteids.* (*F. C. Cook.*)

IN TERMS OF ORIGINAL SAMPLE.

Laboratory number.	Total nitrogen.	Zinc sulphate followed by other reagents.			Phosphotungstic acid followed by other reagents.			Tannin salt followed by other reagents.			Rearrangement of figures for comparison.		
		Zinc sulphate.	Zinc sulphate + phosphotungstic acid.	Zinc sulphate + tannin salt.	Phosphotungstic acid.	Phosphotungstic acid + zinc sulphate.	Phosphotungstic acid + tannin salt.	Tannin salt.	Tannin salt + zinc sulphate.	Tannin salt + phosphotungstic acid.	Zinc sulphate.	Phosphotungstic acid.	Tannin salt.
43	9.66	0.83	3.79	4.30	3.62	4.40	5.47	3.55	3.99	5.55	0.83	3.62	3.55
44	8.25	1.33	4.13	4.45	5.66	5.85	6.24	3.87	4.29	5.87	1.33	5.66	3.87
45	7.57	.88	3.11	3.65	4.48	4.67	4.90	3.04	3.37	4.71	.88	4.48	3.04
46	8.54	.90	4.30	4.05	5.22	5.41	6.07	3.41	3.77	5.57	.90	5.22	3.41
47	4.68	.67	2.15	2.39	2.66	2.77	3.18	1.70	1.90	2.56	.67	2.66	1.70
48	3.10	.08	.62	1.05	1.11	1.16	1.58	.39	.65	1.48	.08	1.11	.39
49	12.38	8.02	11.29	11.77	12.31	12.40	12.47	10.28	11.08	12.15	8.02	12.31	10.28
50	14.20	4.24	13.48	13.99	13.67	13.85	14.18	8.45	11.14	13.50	4.24	13.67	8.45

IN TERMS OF TOTAL NITROGEN.

43	9.66	8.59	39.23	44.51	37.47	45.55	56.62	36.75	41.30	57.45	8.59	37.47	36.75
44	8.25	16.12	50.06	53.94	68.61	70.91	75.64	46.91	52.00	71.15	16.12	68.61	46.91
45	7.57	11.62	41.08	48.22	59.18	61.69	64.73	40.16	44.52	62.22	11.62	59.18	40.16
46	8.54	10.54	50.35	47.42	61.13	63.35	71.08	39.93	44.14	65.22	10.54	61.13	39.93
47	4.68	14.32	45.94	51.07	56.84	59.19	67.95	36.33	40.60	54.70	14.32	56.84	36.32
48	3.10	2.58	20.00	33.87	35.81	37.42	50.97	12.58	20.97	47.74	2.58	35.81	12.58
49	12.38	64.78	91.19	95.08	99.43	100.16	100.73	83.04	89.50	98.14	64.78	99.43	83.04
50	14.20	29.86	94.93	98.52	96.26	97.54	99.86	59.51	78.45	95.07	29.86	96.26	59.51

From these results the following conclusions may be drawn: The sum of the zinc sulphate precipitate and the tannin salt precipitate in the filtrate from the same is higher in all cases but one than the sum of the zinc sulphate precipitate and the phosphotungstic acid precipitate in the filtrate from the same. In the filtrate from phosphotungstic acid the tannin salt reagent precipitates more nitrogen than zinc sulphate. In the filtrate from the tannin salt reagent a larger amount of nitrogen is precipitated by phosphotungstic acid than by zinc sulphate.

The combination precipitating the greatest amount of nitrogen was phosphotungstic acid followed by the tannin salt reagent. The amount of nitrogen precipitated by phosphotungstic acid was greater in each case than that precipitated by any other single reagent.

As was noted last year, the order in which the reagents are employed seems to have an effect on the total nitrogen precipitated by a combination of reagents or by one reagent in the filtrate of another. For instance, more nitrogen was precipitated by phosphotungstic acid followed by zinc sulphate than by zinc sulphate followed by phosphotungstic acid, and by phosphotungstic acid followed by the tannin salt reagent than by the tannin salt reagent followed by phosphotungstic acid. On the other hand, and in this respect the present results do not confirm those of last year, less nitrogen is precipitated by the tannin salt reagent followed by zinc sulphate than by zinc sulphate followed by the tannin salt reagent.

From the previous results reported to the association in 1903 it is believed that no combinations of these reagents will precipitate any of the so-called meat bases, provided that the phosphotungstic acid precipitates be filtered at a temperature not

below 90°. From the present results, confirming in the main those reported a year ago, it is believed that the most complete precipitation of all proteid bodies include albuminoses, and peptones may be obtained by means of phosphotungstic acid followed by tannin salt reagent in the filtrate from the phosphotungstic acid precipitate.

It is also apparent that in the absence of the simpler amids the results obtained by phosphotungstic acid in the cold are practically identical with those precipitated with the same reagent in the hot solution. This relation was evident in the report presented on this subject in 1903. In the presence of notable quantities of the simpler amids Mallet's modification of the phosphotungstic acid method should therefore be employed. In the absence of notable quantities the slight error occasioned by the precipitate of the simpler amids by phosphotungstic acid in the cold may be ignored.

It is believed that if the conditions pointed out in this report are carefully followed, no difficulty will be experienced in getting comparative results with the tannin salt reagent. It is essential that a uniform quantity of sodium chlorid should be employed and that the excess of tannin should not be too great. It has been found, however, that by employing 10 cc of a 10 per cent solution of tannic acid enough of the reagent is present for any commercial meat extract and the excess is not sufficient to occasion material error. The amount of sodium chlorid added should also be governed by the amount of that salt already present in the extract. The method should be studied somewhat more, however, on account of the solubility of the precipitate in the mother liquor. Probably more exact results may be attained by determining the approximate solubility and making a correction for the amount of liquid used. In any case there should be as little liquid employed as possible, and the amount should be uniform.

Although the method for precipitating proteids with zinc sulphate has been carefully studied, and there seems to be no obvious difficulty with the method, results obtained by it do not have the uniformity that is desired. It has been suggested that different results are obtained by different brands of zinc sulphate, and that the amount of precipitate depends to a considerable extent on the purity of the reagent employed. This does not seem probable in view of the large amount of soluble salts present in all brands of meat extract, but the method should be further studied to determine, if possible, the reason for the frequent errors attending its use.

It is recommended that the following methods be added to those adopted by the association for the examination of meat extracts:

Ammonia.—Determine by the magnesium oxid method as described in Bulletin 46, page 21.

Acidity.—Titrate with standard alkali solution, using litmus paper as an indicator. The solution may advantageously be removed from the beaker and placed on the litmus paper by means of a capillary tube.

Phosphorus.—The organic matter should be destroyed by one of the methods given in Bulletin 46, page 12, and phosphoric acid determined by either the gravimetric or volumetric molybdate method described in Bulletin 46, pages 12 and 14.

Chlorin.—Determine chlorin by titration with sulphocyanid according to Volhard. For ordinary purposes the solution of the ash may be employed for this purpose. If exact results are desired, about 1 gram of the meat extract should be dissolved in 20 cc of a 5 per cent solution of sodium carbonate, evaporated to dryness, and thoroughly charred. The residue is then extracted with hot water, filtered, and washed, after which the filter and contents are returned to a platinum dish and ignited. The contents of the dish are then dissolved in nitric acid, added to the filtrate, and the chlorin content determined as indicated above.

Xanthin bases. (*Schittenhelm's method.*)—Dissolve from 3 to 5 grams of extract in 100 cc of water, transfer to a large evaporating dish, and add 500 cc of a 1 per cent

solution of sulphuric acid. Heat on the water bath for 4 or 5 hours, finally evaporating to a volume of from 75 to 100 cc, neutralize with potassium hydroxid, using litmus paper as an indicator. Transfer to a beaker, add 15 cc of a 15 per cent solution of sodium bisulphate and from 15 to 20 cc of a 15 per cent solution of copper sulphate, cover with a watch glass, and let stand over night. Filter and wash with dilute copper sulphate. Return the precipitate to the original beaker, add sodium sulphid, acidify with acetic acid and warm on the steam bath. Filter hot and wash with hot water. Treat the filtrate with 10 cc of 10 per cent hydrochloric acid and evaporate it on the steam bath to about 10 cc. Filter and wash, make ammoniacal, and add in slight excess a 3 per cent solution of ammoniacal silver nitrate. Let stand overnight, filter, wash out all ammonia carefully, and determine nitrogen in the precipitate. The result is the nitrogen of the xanthin bases.

The referee on phosphoric acid presented the following report:

REPORT ON PHOSPHORIC ACID.

By Charles B. Williams, *Referee.*

The work of the referee this year has been confined principally to a study of different methods of effecting solution and determining the total and available phosphoric acid in three samples of Thomas slag. Also, the determinations of their fineness and content of total and soluble lime were made. This work was undertaken in accordance with instructions from the association, looking toward the establishment of some system of valuation of these phosphatic materials based either upon availability or total phosphoric acid content and fineness or both.

It was the original purpose of the referee that pot and field experiments with several phosphatic materials in comparison with basic slags should be conducted this year by the different cooperators, but difficulty in securing phosphatic slags, prepared for fertilizing purposes, delayed sending out the instructions and samples beyond the proper time for beginning these experiments, so that this important part of the proposed work had to be abandoned for this year.

The association, at its last meeting, instructed the present referee to incorporate redonda and precipitated phosphates in his samples for study this year, but this was not done because of his inability to secure samples of these materials.

Some attention was also devoted to the determination of the form and solubility of the lime in the referee's slag samples, because it is believed that the free lime and lime in the forms of carbonate and hydroxid will often possess no small value in increasing plant growth when slags containing considerable quantities of it in these forms are applied to the soil, especially on that large type of soils in some, if not all, of the States in the Union that are distinctly "sour" or acid.

Five samples with the following instructions were sent out to the thirteen chemists who asked for them. At present only results of the work of four laboratories have been reported.

DIRECTIONS FOR PHOSPHORIC ACID WORK FOR THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1904.

I. *Samples.*

Five samples have been collected and prepared for the work this year as follows:
No. 1. American slag.
No. 2. American slag.
No. 3. European slag.
No. 4. Acid phosphate.
No. 5. Cotton-seed meal.

II. *Fineness.*

Shake 10 grams of samples Nos. 1, 2, and 3 in a 100-mesh sieve for ten minutes. Weigh the fine portions that pass the sieve and calculate their percentage respectively of the original samples.

III. *Total phosphoric acid.*

Methods of effecting solution.—Treat 2 grams of samples Nos. 1, 2, and 3 by each solvent given below. Cool, make up to 200 cc with distilled water, and, after standing a sufficient length of time to thoroughly settle, pipette off 20 cc aliquots of each into 16-ounce Erlenmeyer flasks for determination of phosphoric acid, as prescribed in VI.

With those solutions made by hydrochloric acid alone or in excess, add 15 to 20 cc of strong nitric acid to each aliquot portion and evaporate on sand bath to about 15 cc concentration before applying procedure VI.

(a) Hydrochloric acid method: Boil on sand bath with 30 cc of strong hydrochloric acid for 30 minutes, or until the solution has concentrated to about 10 to 15 cc.

(b) Dilute hydrochloric acid method: Dissolve with 30 cc of dilute hydrochloric acid (1 to 1) by boiling on sand bath for about 30 minutes.

(c) Sulphuric acid method: Heat for 30 to 45 minutes on a sand bath with from 10 to 12 cc of concentrated sulphuric acid.

(d) Nitrohydrochloric acid method: Boil on sand bath to about 10 cc concentration with a mixture of 30 cc of strong hydrochloric acid and 10 cc of nitric acid.

IV. *Available phosphoric acid.*

Methods of making solution.—After treating 2 grams by the methods outlined below, filter off two 20 cc aliquots of each solution (which represents 0.2 gram substance in methods (a), (b), (c), and (d), and 0.4 gram in method (e)).

(1) Place one lot in 16-ounce wide-mouth Erlenmeyer flasks; add 30 cc of strong nitric acid and 10 cc of strong hydrochloric acid and boil down on sand bath to about 15 cc concentration. Then apply procedure VI for phosphoric acid determination. (2) To the duplicate lot, after transferring to small platinum dishes, add to each 5 cc of official magnesium nitrate solution, evaporate to dryness over a water bath, and ignite to destroy organic matter. Dissolve in from 10 to 15 cc of dilute hydrochloric acid (1 to 1) and transfer to 16-ounce Erlenmeyer flasks. Measure into each 20 cc of strong nitric acid and boil on a sand bath to about 15 cc concentration. Finish the determination as directed in procedure VI.

(a) Ammonium chlorid citric acid method: Treat samples Nos. 1, 2, and 3 in 16-ounce Erlenmeyer flasks with 100 cc of a 10 per cent solution of ammonium chlorid. Close the flasks securely with rubber stoppers, place in a shaking machine, and shake for 1 hour. Filter and carefully reserve the first 50 cc of each filtrate for lime determination in VII (a). After washing the residues thoroughly with distilled water, remove the filter papers, containing the washed residues, to 16-ounce wide-mouth Erlenmeyer flasks; add 100 cc of a 1 per cent citric acid solution to each; securely stopper and shake the flasks vigorously by hand until the filter papers have been reduced to a fine pulp. Add 100 cc more of the 1 per cent solution of citric acid to each and shake in a shaking machine for 30 minutes at room temperature, noting the same.

(b) Cane sugar citric acid method: Shake samples Nos. 1, 2, and 3 in 200 cc flasks for 30 minutes with 150 cc of a 10 per cent solution of cane sugar; make up to 200 cc and thoroughly mix. Filter off, through dry filter papers, 100 cc of each for lime determinations by VII (b) method; then wash the residues twelve to fifteen times with distilled water and treat with a 1 per cent citric acid solution, as by the above method.

(c) Citric acid method: Wash samples Nos. 1–5 as directed for water-soluble phosphoric acid in Methods of Analysis [a] and reserve filtrates of Nos. 4 and 5 for procedure V. Drop the filters containing the washed residues into 8-ounce Erlenmeyer flasks, into which 200 cc of a 1 per cent solution of citric acid has been previously measured and heated to a temperature of 65° C, and place the flasks, after shaking vigorously to reduce the filter papers to a fine pulp, into a water bath maintained at a temperature of 65° C, and digest for thirty minutes, shaking the flasks

[a] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 46, p. 13.

every five minutes. Then remove the flasks from the bath and cool as quickly as possible to room temperature in a water bath into which cold water is constantly running. After cooling, filter off and treat the filtrates as prescribed in IV (1).

(d) Citric acid method: Treat samples Nos. 4 and 5 with a 1 per cent solution of citric acid as directed in IV (c), except that the citric acid solution and digestion should be at room temperature instead of at 65° C.

(e) Neutral ammonium citrate method: Treat samples Nos. 1–5 exactly as directed in IV (c), except that 100 cc of strictly neutral ammonium citrate solution of 1.09 specific gravity is to be used instead of 200 cc of a 1 per cent citric acid solution.

V. *Water-soluble phosphoric acid.*

Make up reserved filtrates from IV (c) and IV (d) to 400 cc and pipette off 40 cc (equal to 0.2 gram of material) of each solution for determination by procedure VI.

VI. *Volumetric determination.*

Neutralize acidity with ammonium hydroxid and then run in strong nitric acid to slight acidity. Add to each solution about 12 grams of pure ammonium nitrate and make up to a volume of about 40 cc with distilled water. Cool, add 40 cc of recently filtered official molybdic solution and securely stopper with rubber stoppers. Shake the flasks in a shaking machine or by hand for 30 minutes, after which remove and filter through carbon filters by means of suction, using asbestos mats.

After thoroughly transferring the ammonium phosphomolybdate precipitates and washing out the flasks onto the asbestos mats, give the precipitates six more washings each. Then remove the stoppers from the pressure flasks with the small ends of the carbon filters still stuck through them, hold upright over the sink, and wash the outsides free from acid with distilled water. Reverse the carbon filters into the mouths of the flasks which originally contained the precipitates, still holding the small stems, and by means of the copper wires that extend beyond the small ends of the carbon filters, push out the disks, asbestos, and precipitates into the flasks, and wash the disks and inside of carbon filters carefully with a small stream of water. Dissolve the precipitates in a slight excess of standard alkali; add a few drops of phenolphthalein solution to each and titrate back with standard (nitric) acid, using long stirring rods to thoroughly agitate during the operation.[a] The strength of the standard acid and alkali solutions should be made one-half of the strength prescribed in the official volumetric method of the association. Then 1 cc will be equal to one-half milligram of phosphoric acid (0.25 per cent phosphoric acid on basis of 0.2 gram substance taken for analysis).

VII. *Free lime.*

(a) *Ammonium chlorid method.*—To the 50 cc aliquots reserved in IV (a), add ammonium hydroxid in slight excess and boil on sand bath. Filter from any precipitates formed and wash thoroughly with hot water. Evaporate each filtrate to a bulk of about 50 cc and determine the percentage of calcium oxid present by precipitation with ammonium oxalate in the usual way.

(b) *Cane sugar method.*—Titrate the 100 cc aliquots from IV (b) with fifth-normal hydrochloric acid using corallin as an indicator. Divide the number of cubic centimeters of standard acid required by 1.796 to secure the percentage of calcium oxid.

VIII. *Total lime.*

Weigh 2 grams each of samples Nos. 1, 2, and 3 into 200 cc graduated flasks and dissolve by method III (a). Cool, make up to mark and filter off 50 cc in 8-ounce beakers. Precipitate, filter, and wash ferric oxid and alumina in the usual way.[a] Concentrate filtrates over water bath to about 50 cc and determine the percentages of calcium oxid present in each by the regular ammonium oxalate method.[b]

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[a] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 46, pp. 13–14; J. Amer. Chem. Soc., *23*: 8–12.

[b] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 46, pp. 72–73.

Reporting results.

If the collaborator has not sufficient time to perform all the work outlined above, it is especially urged that the degree of fineness and availability of phosphoric acid of samples Nos. 1, 2, and 3 be determined by all the citric acid methods.

In reporting results, note minutely all deviations from the directions of the referee. Work on other samples than those sent out this year will be gladly received and fully credited in the report. All reports should be in the hands of the referee at least thirty days prior to the meeting of the association.

C. B. Williams, *Referee.*
F. P. Veitch, *Associate Referee.*

Total and Available Phosphoric-Acid Results.

The results of this year's work in determining total and available phosphoric acid by the several different tentative methods are given under the proper designations in Tables I, II, III, and IV, which follow.

Table I.—*Total phosphoric acid in Thomas slags by different solvents and its determination volumetrically by precipitation at room temperature with molybdic solution.*

Sample and solvent.	Analyst.			
	F. P. Veitch, D. C.	R. H. Kerr, Md.	F. B. Carpenter,[a] Va.	C. B. Williams, N. C.
Sample No. 1:				
Hydrochloric acid, concentrated		22.15 22.20	21.92	21.65 21.65
Hydrochloric acid, dilute		22.30 22.25	21.95	21.65 21.60
Sulphuric acid, concentrated		22.10 22.00		21.90 21.95
Nitrohydrochloric acid	21.24	21.90 21.80		21.70 21.80
Sample No. 2:				
Hydrochloric acid, concentrated		18.30 18.25	18.27	17.95 17.95
Hydrochloric acid, dilute		18.20 18.20	18.25	17.95 17.85
Sulphuric acid, concentrated		17.95 17.95		18.40 18.30
Nitrohydrochloric acid	17.97	17.85 17.85		18.15 18.10
Sample No. 3:				
Hydrochloric acid, concentrated		17.45 17.55	17.68	17.60 17.50
Hydrochloric acid, dilute		17.50 17.55	17.70	17.55 17.55
Sulphuric acid, concentrated		17.60 17.70		17.75 17.70 17.65
Nitrohydrochloric acid	17.50	17.30 17.40		17.65 17.65

[a] Assisted by S. M. Robinson.

TABLE II.—*Volumetric and gravimetric determination of total phosphoric acid in referee's samples, by F. B. Carpenter and S. M. Robinson.*

Sample and method.	Solvent.			
	III (a).	III (b).	Official.[a] (A_5.)	Official.[a] (A_2.)
Sample No. 1:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Official gravimetric method	22.36	22.23	.....	.....
Official volumetric method	22.15	22.15	.....	.....
Proposed volumetric method	21.92	21.95	.....	.....
Sample No. 2:				
Official gravimetric method	18.59	18.59	.....	.....
Official volumetric method	18.50	18.40	.....	.....
Proposed volumetric method	18.27	18.25	.....	.....
Sample No. 3:				
Official gravimetric method	18.26	18.13	.....	.....
Official volumetric method	18.15	18.18	.....	.....
Proposed volumetric method	17.68	17.70	.....	.....
Sample No. 4:				
Official gravimetric method	.....	.....	15.03 15.08	.....
Official volumetric method	.....	.....	15.10 15.13	.....
Proposed volumetric method	.....	.....	14.88 14.80	.....
Sample No. 5:				
Official gravimetric method	.....	.....	2.81	2.85
Official volumetric method	.....	.....	2.82	2.80
Proposed volumetric method	.....	.....	2.80	2.80

[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. 46, p. 12.

TABLE III.—*Available phosphoric acid as determined by five different methods of treatment.*

SAMPLE No. 1.

Analyst.	Method (a).		Method (b).		Method (c).		Method (d).		Method (e).		Water-soluble P_2O_5.
	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
F. P. Veitch, U. S. Department of Agriculture	10.19	.....	.....	.....	8.12	.....	.....	.....	6.99	.....	.....
R. H. Kerr,[a] Maryland Agricultural College	9.40	9.10	8.45	8.45	7.65	.....	6.80	.....	6.53	6.53	.....
	9.40	8.95	8.35	8.40	7.55	7.80	6.60	6.70	6.48	6.55	.....
C. B. Williams,[b] North Carolina Department of Agriculture	9.75	9.62	8.10	8.08	.....	.....	.....	.....	.....	.....	.....
	9.72	9.68	8.15	8.00	8.12	.....	.....	.....	.....	6.44	.....
Average	9.69	9.34	8.24	8.23	7.86	7.80	6.70	6.70	6.67	6.51	.....

[a] Room temperature for method (a) 25° C; (b) 22° C; and (d) 22° C.
[b] Room temperature for method (a) 30° C; (b) 30° C; and (d) 24° C.

TABLE III.—*Available phosphoric acid as determined by five different methods of treatment*—Continued.

SAMPLE No. 2.

Analyst.	Method (a).		Method (b).		Method (c).		Method (d).		Method (e).		Water-soluble P_2O_5.
	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	30 cc HNO_3 + 10 cc HCl. (1)	Mg $(NO_3)_2$ ignition. (2)	
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
F. P. Veitch, U. S. Department of Agriculture	10.67	.....	.....	.....	8.30	.....	.....	.....	7.47	.....	.....
R. H. Kerr, Maryland Agricultural College	.....	.....	.....	.....	7.30	.....	5.65	5.70	6.10	.....	.....
	9.50	9.65	8.70	8.70	7.20	7.20	5.70	5.75	6.13	6.20	.....
C. B. Williams, North Carolina Department of Agriculture	9.80	9.90	8.22	8.18	.....	.....	.....	.....	.....	.....	.....
	9.78	9.85	8.20	8.20	8.42	.....	.....	.....	6.01	6.16	.....
Average	9.94	9.80	8.37	8.36	7.80	7.20	5.67	5.73	6.08	6.18	.....

SAMPLE No. 3.

F. P. Veitch, U. S. Department of Agriculture	14.38	.....	.....	.....	10.55	.....	.....	.....	8.13	.....	.....
R. H. Kerr, Maryland Agricultural College	14.00	.....	11.20	10.50	9.60	.....	.....	8.10	7.80	.....	.....
	13.90	13.75	10.55	11.00	9.40	9.35	8.10	8.15	7.83	7.73	.....
C. B. Williams, North Carolina Department of Agriculture	.....	13.93	10.72	10.62	.....	.....	.....	.....	.....	.....	.....
	14.00	13.98	10.67	10.68	9.98	.....	.....	.....	7.82	7.88	.....
Average	14.07	13.89	10.79	10.70	9.66	9.35	8.10	8.13	7.90	7.81	.....

SAMPLE No. 4.

F. P. Veitch, U. S. Department of Agriculture	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
R. H. Kerr, Maryland Agricultural College	.....	.....	.....	.....	3.75	.....	1.70	1.60	.....	.....	10.25
	.....	.....	.....	.....	3.65	3.55	1.60	1.65	4.30	4.28	10.25
C. B. Williams, North Carolina Department of Agriculture	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	10.05
	.....	.....	.....	.....	4.18	.....	2.08	.....	.....	4.50	10.10
Average	.....	.....	.....	.....	3.86	3.55	1.79	1.63	4.30	4.39	10.16

SAMPLE No. 5.

F. P. Veitch, U. S. Department of Agriculture	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
R. H. Kerr, Maryland Agricultural College	.....	.....	.....	.....	0.08	.....	0.20	0.20	.....	.....	0.60
	.....	.....	.....	.....	.08	0.08	.20	.20	1.05	1.15	.65
C. B. Williams, North Carolina Department of Agriculture	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.48
	.....	.....	.....	.....	.12	.09	.28	.25	.....	1.10	.50
Average	.....	.....	.....	.....	.09	.09	.23	.22	1.05	1.13	.56

As an average of all results by the different methods of solution it is found that slag samples Nos. 1, 2, and 3 contain 21.89, 18.09, and 17.59 per cent of total phosphoric acid, respectively. When these percentages for the different samples are divided into their respective percentages of available phosphoric acid we have the following results:

TABLE IV.—*Total phosphoric acid shown available by five methods of treatment.*

Sample No.	Method—				
	(a).	(b).	(c).	(d).	(e).
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	43.4	37.6	35.8	30.6	30.1
2	54.5	46.2	41.4	31.5	33.9
3	79.5	61.1	54.1	46.1	44.6

FINENESS.

Samples Nos. 1 and 2 are American slags, and No. 3 a European product. No. 2 was prepared in the laboratory of the North Carolina department of agriculture by grinding crude slag until it would pass a 0.5 mm sieve, while Nos. 1 and 3 were taken from sacks placed on sale in the market of this country as fertilizing materials.

TABLE V.—*Percentages of fine and coarse particles of three samples of Thomas slag.*

Analyst.	Sample No. 1.		Sample No. 2.		Sample No. 3.	
	Fine.	Coarse.	Fine.	Coarse.	Fine.	Coarse.
F. P. Veitch, U. S. Department of Agriculture	87.83	12.17	65.98	34.02	84.30	15.70
R. H. Kerr, Maryland Agricultural College	73.40	26.60	60.80	39.20	78.50	21.50
C. B. Williams, North Carolina Department of Agriculture	86.45	13.55	64.34	35.66	83.28	16.72
	86.02	13.98	64.16	35.84	83.22	16.78
	86.23	13.77	63.88	36.12	83.78	16.22

NOTES AND COMMENTS BY ANALYSTS.

R. H. Kerr.—The instructions have been strictly followed by me except that the regular official volumetric method of the association was used in determining available phosphoric acid in the solutions made by procedures (c), (d), and (e). For the others the method of precipitation and filtration given in the instructions was used, carbon filters being improvised by cutting off a pair of large, fat-extraction tubes. They worked very nicely, but I found the official method much faster and so used it for the latter part of the work. I used a wooden frame 100-mesh sieve, 8 inches in diameter, for getting the percentage of fine material in the three slag samples, but I am sure a small amount of the fine material was not determined.

F. B. Carpenter and S. M. Robinson.—You will note that we have made total phosphoric acid on all the samples by the official gravimetric method, official volumetric method, and the volumetric method, carried out according to your instructions.

The volumetric method as proposed by you gives materially lower results than either the official volumetric or the official gravimetric methods. We found 0.60 per cent insoluble and 14.52 per cent available phosphoric acid in sample No. 4, and 0.14 per cent insoluble and 2.67 per cent available in sample No. 5 when determined by the official volumetric method of the association.

F. P. Veitch.—The prescribed methods were followed in all essential details.

On total phosphoric acid I obtained the same results by the gravimetric method when the yellow precipitate was dissolved and reprecipitated before precipitation with magnesia mixture, as by the volumetric method, except on sample No. 2, where the difference was 1 per cent. As I was too busy to repeat the gravimetric work the results are not submitted.

Referee.—Results obtained by myself and other workers in this laboratory in the determination of total lime in samples Nos. 1, 2, and 3 were not incorporated in Table VI because of the great divergence in duplicate results, even when measured from the same solution and worked apparently under identical conditions. Duplicates in the same set and from the same solution varied as much as 3 to 4 per cent of lime. It was thought at first that possibly these differences were due to silica being carried down with the calcium oxalate; but in subsequent sets of duplicates of all three samples in which the solutions, after elimination of ferric oxid and alumina, were evaporated to dryness over a water bath and the residues then heated in an air bath for five hours at about 110° C, it was found that when the residues were taken up with dilute hydrochloric acid in the usual way there was no undissolved portion in any of the solutions. Pressure of other work has prevented the referee from further investigation of the cause of the difficulty.

In determining available phosphoric acid by method (e), the referee found considerable difficulty in getting the phosphoric acid to precipitate if the samples were not treated by the magnesium nitrate-ignition procedure. One could never be certain with the nitrohydrochloric-acid treatment that all the phosphoric acid would precipitate.

Discussion of Results.

Total phosphoric acid.—The total phosphoric-acid results on the three slag samples by each analyst are very concordant for each method of solution, but there is often considerable variation between the results of different analysts and between the results of the same analysts obtained on the same sample by different solvents. The referee found that the concentrated sulphuric acid method (II c) gave higher results in his hands than any of the other methods suggested, but also found that any of the other methods were more satisfactory to work with. In the sulphuric-acid method a large amount of calcium sulphate is formed which is often hard to manage.

Available phosphoric acid.—Here, as with total phosphoric acid, there is often considerable variation between the results of the different workers with the same method on the same sample. The ammonium-chlorid citric acid and the cane-sugar citric acid methods were the two which acted most energetically upon the slags; but as we have data from neither field nor pot tests, it is impossible to say which one of all the solvents comes nearest to representing what different plants will be able to do with an application of this material on different soils for an average season.[a]

Sample No. 1, which contains a higher percentage of fine material passing the 100-mesh sieve than either of the two other slags, is the one that shows the lowest percentage of total phosphoric acid available by every one of the solvents tested. No. 2, the coarsest sample, is second in availability of phosphoric acid, while No. 3, a European slag, possesses the highest solubility. It is quite evident from these results that some one or more different conditions in the make-up of some slags render their phosphoric acid more readily attacked by the weak organic solvents than that contained in others of the same or greater degree of fineness. European slag, No. 3, not only shows a greater coefficient of solubility of its phosphoric-acid content than

[a] The North Carolina department of agriculture has some plat experiments with slag that have been running 2 years the results of which will be published during the coming year.

either of the American slags, but also possesses a higher percentage of available lime, as shown by treatment with 10 per cent solution of ammonium chlorid. The latter fact may have an important bearing in the explanation of the high percentage available of the total phosphoric acid in this sample. Wagner[a] found, in some investigations which he carried on with Thomas slags from different sources, that those which contained the highest percentage of silica were the ones that gave the highest availability of phosphoric acid to citrate solution. As sufficient spare time was not available for the referee to determine the percentage of silica in the referee's slag samples, he is not in a position to say whether or not the results obtained on samples Nos. 1, 2, and 3 confirm or controvert the results of Wagner.

Lime in basic slags.—Results obtained in the determination of total and available lime with samples Nos. 1, 2, and 3 are brought together in Table VI:

TABLE VI.—*Total and available lime in basic slags.*

Analyst.	No. 1.				No. 2.				No. 3.			
	Lime dissolved.				Lime dissolved.				Lime dissolved.			
	By 10 per cent ammonium chlorid solution.	By 10 per cent cane sugar solution.	By distilled water.	Total lime.	By 10 per cent ammonium chlorid solution.	By 10 per cent cane sugar solution.	By distilled water.	Total lime.	By 10 per cent ammonium chlorid solution.	By 10 per cent cane sugar solution.	By distilled water.	Total lime.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
F. P. Veitch, U. S. Department of Agriculture	6.40	.....	1.10	.....	6.99	.....	2.04	.....	7.75	.....	1.22	.....
R. H. Kerr, Maryland Agricultural College.	.....	1.34	.....	29.43	7.48	2.73	.....	.....	8.42	1.12	.....	.....
	7.38	1.39	.....	29.63	7.58	2.78	.....	29.53	8.38	1.17	.....	25.85
C. B. Williams, North Carolina Department of Agriculture	6.71 6.76 6.73 6.82	.....	.....	.....	7.21 7.20	.....	.....	.....	8.18 8.15	.....	.....	.....

The duplicate results secured in the determination of available lime by the 10 per cent ammonium chlorid method are tolerably concordant for each worker, but the results of the different analysts upon comparison show but little agreement. Your referee is of the opinion that results by the ammonium chlorid method more nearly represent the available lime in the slag samples tested than either of the other two methods. Paturel[b] found that dilute ammonium chlorid solution dissolved all the free lime in slags without attacking that in the form of silicate and phosphate. The 10 per cent cane sugar solution seemed to act but little, if any, more energetically than ordinary distilled water.

RECOMMENDATIONS.

It is recommended:

(1) That the referee for next year plan field and pot experiments with cultivated plants, looking toward the establishing of the relative value of the total phosphoric-acid content of basic phosphate slags (both foreign and domestic), redonda and precipitated phosphates, of different degrees of fineness, in comparison with the

[a] Chem. Ztg., No. 79, *18*: 1511.

[b] Ann. Agron., No. 11, *22*: 497–515; Bul. soc. chim., Paris, vol. 17–18, No. 5, pp. 319–321 (through Exper. Sta. Rec., *8*: 681–682).

phosphoric acid contained in acid phosphate and other common phosphatic materials found on sale in our markets, and invite cooperation on as many different soil types and by as many workers as possible.

(2) That further study be made of the methods for determining total and available lime contained in basic phosphatic slags.

(3) That a study of the methods for determining total phosphoric acid in basic phosphatic slags be continued.

(4) That the referee for next year make a study of the solubility of the phosphoric acid in samples of the same slag of different degrees of fineness.

In connection with the report on phosphoric acid Mr. Wheeler submitted by title the following paper:

THE EFFECT UPON THE RESIDUE, AFTER EXTRACTING THE SOLUBLE PHOSPHORIC ACID, OF POSTPONING THE TREATMENT WITH AMMONIUM CITRATE.

By B. L. Hartwell and J. W. Kellogg.

It has been the custom at the Rhode Island station to make the determinations of soluble phosphoric acid in fertilizers, and to treat the residues from the same with ammonium citrate, in all of the samples soon after they are collected. The air-dried residues from the ammonium citrate treatment are placed in small, turned wooden boxes and the determinations of the phosphoric acid in the same (insoluble phosphoric acid) made later at any convenient time.

This course has been pursued in order to avoid the changes in the amounts of the soluble, reverted, and insoluble phosphoric acid which usually take place upon standing. Such a plan becomes necessary, when several months elapse before the fertilizer analyses are completed, in order that the amounts of the different forms of phosphoric acid found by analysis shall correspond with those actually present at the time the fertilizers were used.

The principal objection to this method of procedure is that it delays the completion of the analysis of any of the fertilizers whose publication it may be desired to hasten.

It seemed probable that if the soluble phosphoric acid were removed promptly and the residues thoroughly air-dried, it would not be necessary, in order to guard against changes in the amount of insoluble phosphoric acid, to extract the reverted acid until later, whenever it was convenient. The present work was undertaken to secure some evidence on this point.

Two portions of 2 grams each, taken from the individual samples, were both extracted with water in the usual manner to remove the soluble phosphoric acid, and the residues were dried in the air. Only one of the residues in each case was treated promptly, within a day or two, with the ammonium citrate solution to remove the reverted phosphoric acid. The residues from this treatment, as well as those from the portions which had been extracted with water only, were placed in the wooden boxes. After about 15 weeks the residues from the extraction with water only were digested with the ammonium citrate solution and the insoluble phosphoric acid determined at once. At the same time the phosphoric acid was determined in the residues from the earlier treatment with ammonium citrate. The determinations from each solution were repeated upon subsequent days and the results (b) are placed beside the first determinations (a) from the same solutions.

The weights of magnesium pyro-phosphate in grams, representing the insoluble phosphoric acid per one-half gram of fertilizer, are given below:

TABLE I.—*Insoluble phosphoric acid per half gram of fertilizer expressed as magnesium pyro-phosphate.*

Number of sample.	Series I. Early extraction of the "reverted."		Series II. "Reverted" extracted about 15 weeks later.		Difference between Series I and Series II.
	a.	b.	a.	b.	
	Gram.	*Gram.*	*Gram.*	*Gram.*	*Gram.*
1	0.0080	0.0084	0.0080	0.0073	−0.0005
2	.0187	.0185	.0179	.0180	− .0004
3	.0113	.0114	.0121	.0122	+ .0008
4	.0142	.0142	.0149	.0148	+ .0007
5	.0178	.0177	.0195	.0177	− .0008
6	.0244	.0245	.0223	.0223	− .0022
7	.0181	.0182	.0184	.0177	− .0001
8	.0075	.0077	.0081	.0078	− .0004
9	.0125	.0124	.0124	.0119	− .0003
10	.0122	.0125	.0135	.0134	+ .0011
11	.0163	.0163	.0167	.0160	+ .0001
12	.0135	.0142	.0147	.0146	+ .0008
13	.0237	.0236	.0233	.0228	− .0004
14	.0156	.0156	.0162	.0164	+ .0007
15	.0160	.0160	.0138	.0134	− .0024
16	.0137	.0139	.0143	.0138	+ .0003
17	.0264	.0258	.0209	.0207	− .0053

Before drawing any conclusions from the above differences, it is necessary to know how wide a variation is liable to occur, in routine work, between two determinations of insoluble phosphoric acid in a given sample under our conditions, where the extractions of the soluble and of the reverted phosphoric acid are made upon different days from separate portions of the sample, and where a single result only is secured from each residue containing the insoluble phosphoric acid. From an inspection of a large number of results it was found that the difference was rarely *greater* than 1.5 milligrams (0.19 per cent), being in most cases much less. It may be seen from the above results that in the cases of Nos. 6, 15, and 17 only was this limit exceeded; so that the differences in the remaining instances must be considered as falling within the limit of error *liable* to occur under the conditions of the work.

Whether the reduction in amount of insoluble phosphoric acid in Nos. 6, 15, and 17 was actually caused by the postponement of the ammonium citrate extraction, as is indicated by the results, or to unknown causes could only be ascertained with certainty by a larger number of determinations. If it should be proved that there is in certain isolated cases somewhat less insoluble phosphoric acid when the extraction with ammonium citrate is postponed for several months, no injustice would be done to the manufacturer, as the available phosphoric acid would become correspondingly greater.

It is interesting to note that considering all the other numbers together there is a *tendency* toward an increased amount of insoluble phosphoric acid in the residue from the later extraction with ammonium citrate, although the difference in every case is within the limit of error. It is not improbable that any difference which might occur would be plus or minus, depending upon the nature of the fertilizer.

It is realized that the results herein recorded do not settle the question under consideration; but they indicate that no large error will arise if, for the sake of greater

convenience, the dried residues from the extraction with water are kept a number of weeks before the "reverted" phosphoric acid is removed by the ammonium citrate.

A discussion on the availability of phosphoric acid in fertilizers and the value of basic slag and redonda phosphates followed, in which Messrs. Veitch, Wheeler, Huston, Hobbs, W. J. Jones, and Browne took part. At the close of the discussion the report of the referee on medicinal plants and drugs was received.

REPORT ON MEDICINAL PLANTS AND DRUGS.

By L. F. Kebler, *Referee.*

This report brings to the association a line of work which in a measure differs from the usual themes considered, yet the principles underlying the chemical analysis are the same as obtain in other branches of chemical investigations, and the excellent methods governing the workings of this association should be of great service in establishing and unifying analytical methods for plants and drugs, which would undoubtedly be instrumental in developing and extending an industry at present greatly neglected in this country. Many of the State legislatures have passed laws authorizing the examination of medicinal remedies from time to time, and judging from the activities manifested in certain States, members of this association may expect to be called on at any time to investigate these products. The United States Pharmacopœia is usually specified as the standard for this purpose. Until recently, however, this authority has had little weight legally, although highly respected and voluntarily made the standard by many druggists and manufacturing houses of this country.

In some cases large manufacturers have found that certain analytical methods are more expeditious and give more uniform and satisfactory results than those prescribed by the Pharmacopœia, and it is only natural that they should adopt such methods for assaying crude drugs and adjusting the strengths of the various preparations made by them. The present edition of the Pharmacopœia, moreover, provides standards and analytical methods only for a few of the many potent plant drugs recognized and preparations derived from the same, but most progressive manufacturers have adopted their own standards and methods for determining the same for many other potent drugs. Undoubtedly the next edition of the Pharmacopœia will contain standards for most of the highly potent remedies and provide methods for determining the same. Such methods should be used whenever practicable, even at a little inconvenience and increase in cost, but the referee can not see any good reason why a manufacturer should not use his own methods for adjusting the strengths of his preparations provided such preparations comply with the pharmacopœial standards when analysed by the pharmacopœial methods.

The various progressive pharmacopœias usually contain different analytical methods for arriving at the strengths and medicinal values of crude drugs and their preparations. The methods used by the different port chemists and analysts in this and other countries vary according to the several governing local authorities. When it is called to mind that analysts using the same method and material frequently report results that are far from satisfactory it should not be surprising that various workers, using entirely different methods, obtain very discordant results. Transactions of considerable magnitude are frequently made on the basis of a given amount of a certain chemical constituent. It can therefore readily be seen that if the results of the chemists employed by the buyer and seller do not agree within reasonable limits, complications are likely to arise. The sample may be referred to a third analyst only with the result that still greater confusion is introduced. It sometimes happens that in settling a dispute of this kind the chemists' results are

set aside entirely. Men of affairs naturally discredit the chemists' usefulness when the results obtained differ so materially as to render them useless for commercial transactions. It is at times impossible to explain the cause of existing discrepancies, as merchants usually have no knowledge of chemical methods and the occurrence of discordant results due to the use of different methods is incomprehensible to them. For these reasons chemists always welcome improvements in analytical methods and unification of the same.

Opium is the most important of all drugs, considered medicinally and commercially. It is customary to sell and buy this article on the percentage content of morphine. Small differences in the per cent of morphine reported by various analysts frequently involve considerable money, and every possible effort should be made to reduce such inequalities to a minimum. During the past few years quite a widespread controversy has taken place in this country relative to the most efficient method for estimating morphine in opium. One faction contended that the present pharmacopœial method, with a correction for the morphine, is the most satisfactory for the present, while the other faction claimed that a modified lime method would be more suitable and give results nearer the truth. It appears to the referee that what is really needed is a method that will give fairly concordant results in the hands of chemists. With this end in view the following directions for cooperative work were sent out:

At the Twentieth Annual Convention of the Association of Official Agricultural Chemists, 1903, a referee on medicinal plants and drugs was appointed. The immediate object of this appointment is a collaborative, systematic study of the analytical methods used in determining the quality of crude plants, drugs, and products derived from them with a view to improving and ultimately unifying the methods of analyses for such substances. The earnest cooperation of every chemist interested in this line of work is most cordially invited. The referee will take pleasure in sending samples for analysis to all who inform him on or before April 11 of their willingness to cooperate in the work.

The work this year will be confined to powdered opium, and the methods to be studied at this time are those considered to be among the best. Suggestions for new methods or improvements on old processes will be gladly received and given an impartial trial next year or at an earlier date if possible. The results should be in the referee's hands not later than August 15, 1904.

POWDERED OPIUM.

Method I.—United States Pharmacopœia, 1890, with Additions.

Run two sets of duplicates on opium as received and report results for each set. Also weigh the crystals in the inner filter counterpoised by the outer filter and report results. Intimately mix the morphine of each set and test them as follows:

(1) Dry 0.5 gram at 110° C to constant weight and note per cent of loss.

(2) To 0.5 gram of morphine, dried at 60° C, add 18 cc of decinormal sulphuric acid, warm slightly to bring about a complete combination of the alkaloid and acid and add 50 cc of distilled water and 5 drops of cochineal solution (prepared according to Sutton's Volumetric Analysis, from pure cochineal). Then titrate back the excess of acid with N/40 potassium hydrate solution. Each cubic centimeter of decinormal sulphuric acid solution represents 30.23 mgs of crystallized morphine. Report per cent of purity.

(3) In a 100 cc glass-stoppered cylinder place exactly 0.5 gram of crystallized morphine; add 25 cc of decinormal potassium hydroxid and shake thoroughly at intervals until the crystals are disintegrated. Dilute to 100 cc with neutral distilled water, mix thoroughly, filter and to 50 cc of the filtrate add 25 cc of decinormal sulphuric acid and 5 drops of cochineal solution. Titrate back the excess of acid with N/40 potassium hydroxid solution. Each 50 cc of the above filtrate contain 0.25 gram of morphine and 12.5 cc of decinormal potassium hydroxid solution. The amount of acid in excess of that required to neutralize the alkali in the filtrate and the alkali added to titrate back the excess of acid is combined with the alkaloid. Each cubic centimeter of decinormal acid represents 30.23 mgs of crystallized morphine. Report per cent of purity.

Place 0.5 gram of the morphine in a graduated, glass-stoppered cylinder, carefully add, by pouring down the side of the inclined cylinder, 50 cc of good lime water, stopper the cylinder and agitate its contents by cautiously tilting backward and forward, so as to avoid the formation of a froth on the surface. The agitation is to be continued until complete solution results or the particles cease to diminish in size. The solution is then filtered through a pair of counterpoised filters about 7 cm in diameter, the residue and filters being well washed with 5 cc of lime water, and then with 5 cc of water. When drained the filters are closed, pressed between bibulous paper, dried to constant weight at 100° C, and weighed. The difference in the weight of the two filter papers is the amount of foreign material, insoluble in lime water, which is associated with the morphine. Report purity of morphine by this method.

Method II.—Lime method, United States Pharmacopœia, 1880, and British Pharmacopœia, 1898, modified.

In a 250 cc Florence flask or suitable bottle place 14 grams of opium and 6 grams of slacked lime. (Prepare the lime by mixing in a beaker, with constant stirring, 10 grams of good quality powdered quicklime and 5 cc of water; when the reaction is completed set aside to cool.) Mix the lime and opium thoroughly, and gradually add 140 cc of water in small portions and with frequent agitations. Stopper the flask and shake occasionally with a rotatory motion during 2 hours. Filter through a dry 10 cm plaited filter. Transfer exactly 104 cc (representing 10 grams of opium) of the filtrate to a 250 cc Florence flask or suitable bottle, add 10 cc of ethyl alcohol (about 95 per cent) and 50 cc of ether (specific gravity 0.725 at 15° C). Shake the mixture, add 4 grams of ammonium chlorid, shake vigorously for 5 minutes, then shake well at intervals during one-half hour and set aside in a cool place for 12 hours for the morphine to separate. Counterpoise two 9 cm filters, placing one within the other on the funnel in such a way that the triple fold of the inner one is laid against the single fold of the outer; moisten them with ether and transfer the ethereal layer in the flask to the filter either by careful decantation or by means of a pipette. Add 10 cc of ether to the flask, rotate it carefully and allow it to stand a few minutes before decanting the ethereal layer onto the filter. Repeat this operation with 10 cc more of ether. Let the filter air dry and then pour onto it the contents of the flask in portions in such a way as to transfer the greater part of the crystals to the filter. When the liquor has passed through, transfer the remaining crystals to the filter by washing with several portions of water saturated with powdered morphine, using not more than 20 cc of the morphinated water in all. Allow the double filter to drain, then apply morphinated water to the crystals, drop by drop, until they are practically free from mother-liquor; finally wash them, drop by drop, with alcohol previously saturated with powdered morphine until the washings are free from color. When the alcohol has passed through displace the adhering alcohol by ether, using about 10 cc, or more if necessary. Allow the filter to dry to constant weight at a temperature not exceeding 60° C. Weigh the crystals in the inner filter counterpoised by the outer filter, then carefully transfer the crystals to a tared watch-glass and weigh again. Report both weighings.

Test the morphine for purity, etc., as directed under Method I, and report results.

Method III.—Stevens.

Triturate 4 grams of opium in a mortar with 2 grams of fresh oxid of lime (not air-slacked) and 10 cc of water until a uniform mixture results. Add 19 cc of water and stir frequently for half an hour. Filter through a dry filter about 10 cm in diameter and transfer exactly 15 cc to a 60 cc bottle. To this add 4 cc of alcohol and 10 cc of ether and shake the mixture; then add 0.5 gram of ammonium chlorid. Shake well and frequently during half an hour and set aside in a cool place for 12 hours.

Remove the stopper carefully and preserve, with any adhering crystals, for future use. Pour the ethereal layer into a small funnel the neck of which has been previously closed with a piece of absorbent cotton. Rinse the bottle with 10 cc of ether, and when this has passed through pour the contents of the bottle into the funnel. Without trying to remove all of the crystals from the bottle, wash the bottle and the contents of the funnel with morphinated water until the washings are colorless. When the crystals have drained, place the stem of the funnel in the bottle containing adhering crystals and with a small glass rod, drawn out to a curved point, lift the cotton and rinse the crystals into the bottle with 12 cc of decinormal sulphuric acid, using the cotton on the end of the rod to detach any adhering crystals. Place the

cotton in the bottle, replace the cork, and agitate until the crystals are all dissolved. Rinse the cork and funnel with water and titrate the excess of acid with N/40 potassium hydroxid.

The number of cubic centimeters of decinormal acid consumed by the morphine, multiplied by 1.5038, will give the percentage of morphine obtained, to which add 1.12 as a correction for the morphine remaining in the solution.

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Referee, Medicinal Plants and Drugs.

WASHINGTON, D. C., *March 30, 1904.*

The above instructions were sent to fifty different chemists and manufacturing houses. Ten favorable responses were received, and it gives the referee pleasure to be able to report that all the results were sent in promptly with the exception of those of one chemist, who was unable to do the work on account of illness. This certainly speaks well for the interest manifested in this investigation, but it is hoped that a greater number will take part in future cooperative work of this character. It is the referee's intention, as soon as it is feasible, to have appointed a number of associate referees to take up certain lines of work, and every university, college of pharmacy, manufacturing house, board of health, board of pharmacy, and the individual chemists should take some part in the work.

The powdered opium sent out for analysis was taken from a 5-pound container which was purchased on the open market. The opium was thoroughly mixed at the drug laboratory before being sent out, so that all samples were of uniform composition. The label on the can stated that the opium contained 14.01 per cent of morphine. Physically it was of good quality. The results obtained by the various workers are contained in the following tables:

TABLE I.—*Results of cooperative work on opium, Method I, United States Pharmacopœia, 1890, with additions.*

Name.	Amount of morphine on filter paper.	Average.	Amount of morphine on watch glass.	Average.	Purity by acid titration.	Purity by KOH or Lyons's method.	Purity by lime water.	Morphine in opium by acid titration.[a]	Morphine in opium by KOH or Lyons's method.[a]	Morphine in opium by lime water.[a]	Moisture in morphine at 110° C.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Blome	13.56	13.59	13.46	13.477	96.916	92.22	94.76	13.06	12.43	12.71	5.5
Do	13.63		13.495								
Do	[c]14.75	[b][c]14.80	[c]14.70	[c]14.75	[c]94.94	[c]90.47	[c]85.86	[c]14.00	[c]13.34	[c]12.66	5.92
Do	[c]14.85		[c]14.80								
Dohme	13.59	13.47	13.36	13.30	98.64	94.83	95.98	13.12	12.61	12.77	6.8
Do	13.36		13.24								
Do	13.65	13.64	13.49	13.46	98.41	95.22	94.60	13.25	12.82	12.73	6.53
Do	13.64		13.44								
Doolittle	[c]9.786	[c]9.75	[c]9.69	[c]9.64	98.55	98.61	.....	.....	.....	.....	6.64
Do	[c]9.715		[c]9.60								
Havenhill	14.31	13.97	14.305	13.947	[d]96.91	[d]93.16	[d]91.80	13.49	12.96	12.78	[d]6.74
Do	13.63		13.53								
Do	14.24	14.097	14.12	13.99	[d]96.91	[d]93.16	[d]91.80	13.56	13.03	12.84	[d]6.74
Do	13.955		13.87								
Kebler	13.61	13.55	13.50	13.43	96.60	91.98	94.60	12.97	12.35	12.70	7.05
Do	13.50		13.37								
Do	13.54	13.51	13.45	13.41	97.00	93.08	96.64	13.01	12.48	12.96	6.90
Do	13.48		13.36								

TABLE I.—*Results of cooperative work on opium, Method I, United States Pharmacopœia, 1890, with additions*—Continued.

Name.	Amount of morphine on filter paper.	Average.	Amount of morphine on watch glass.	Average.	Purity by acid titration.	Purity by KOH or Lyons's method.	Purity by lime water.	Morphine in opium by acid titration.	Morphine in opium by KOH or Lyons's method.[a]	Morphine in opium by lime water.[a]	Moisture in morphine at 110° C.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Lyons	13.81	13.77	13.68	13.64	[e]97.91	[e]93.57	95.65	13.35	12.76	13.05	6.6
Do	13.74		13.61								
Mallinckrodt Chemical Works	14.36	14.30	14.19	14.25	94.41	91.03	89.20	13.45	12.97	12.71	6.6
Do	14.24		14.31								
Do	13.78	[f]14.01	13.73	13.96	97.36	92.63	92.10	13.59	12.93	12.86	6.96
Do	14.25		14.19								
Puckner	13.70	13.52	13.47	13.21	97.11	92.41	94.94	12.83	12.21	12.54	.....
Do	13.35		12.95		96.37	91.39	89.60	12.73	12.07	11.84	.....
Do	[g]13.90	14.16	13.83	14.09	96.50	92.92	91.44	13.60	13.09	12.88	6.88
Do	[g]14.42		14.35		96.64	93.84	86.33	13.62	13.22	12.16	7.07
Ruddiman	14.21	14.09	14.09	14.04	97.32	88.53	.....	13.66	12.43	.....	7.10
Do	13.98		14.00								
Do	14.30	14.25	14.24	14.20	96.41	88.53	91.30	13.69	12.57	12.96	7.06
Do	14.21		14.16								
Smith	[c]14.58	[c]14.62	[c]14.50	[c]14.55	96.42	97.02	96.00	[c]14.03	[c]14.12	[c]13.97	6.06
Do	[c]14.67		[c]14.60								
Do	[c]14.59	[c]14.62	[c]14.53	[c]14.58	96.41	97.02	95.90	[c]14.06	[c]14.15	[c]13.98	6.10
Do	[c]14.66		[c]14.63								
Average	.....	13.85	.....	13.74	96.99	93.22	93.04	13.31	12.68	12.70	6.62
Maximum	14.42	14.30	14.35	14.25	98.64	98.61	96.64	13.69	13.22	13.05	7.10
Minimum	13.35	13.47	12.95	13.21	94.41	88.53	86.33	12.73	12.07	11.84	5.50
Difference	1.07	.83	1.40	1.04	4.23	10.08	10.31	1.96	1.15	1.21	1.60

[a] Based on per cent of morphine weighed on watch glass.
[b] Stood twenty-four hours before separating morphine.
[c] Not included in average, maximum and minimum.
[d] Results obtained by mixing morphine of both sets of duplicates.
[e] Acid standardized against morphine.
[f] Per cent of morphine by Mallinckrodt's method, 12.92.
[g] Used porcelain gooch crucible, provided with paper disk, all dried to constant weight.

TABLE II.—*Results of cooperative work on opium, Method II, United States Pharmacopœia, 1880, modified.*

Name.	Amount of morphine on filter.	Average.	Amount of morphine on watch glass.	Average.	Purity by acid titration.	Purity by KOH, or Lyons's method.	Purity by lime water.	Morphine in opium by acid titration.[a]	Morphine in opium by KOH, or Lyons's method.[a]	Morphine in opium by lime water.[a]	Moisture in morphine at 110° C.
	Per cent.	*Per ct.*	*Per cent.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Blome	11.698	11.61	11.59	11.512	96.00	97.12	93.4	11.05	11.18	10.75	6.46
Do	11.523		11.435								
Do	11.70	11.70	11.60	11.60	98.206	98.03	99.37	11.39	11.37	11.53	6.63
Dohme	11.87	11.90	11.81	11.78	98.76	98.25	99.2	11.63	11.57	11.69	7.00
Do	11.93		11.75								
Do	11.22	11.43	11.05	11.26	98.77	98.40	99.6	11.12	11.08	11.21	6.6
Do	11.64		11.48								
Doolittle	[b] 9.396	[b] 9.554	[b] 9.33	[b] 9.462	99.51	96.60	.....	[b] 9.42	[b] 9.14	.....	6.32
Do	[b] 9.712		[b] 9.594								
Havenhill	11.25	11.235	11.21	11.177	.....	.....	[c] 99.99	.....	.....	11.17	6.62
Do	11.22		11.14								
Do	11.33	11.42	11.267	11.333	.....	.....	[c] 99.99	.....	.....	11.33	6.62
Do	11.51		11.40								
Kebler	11.46	11.35	11.33	11.25	98.75	97.62	99.10	11.11	10.98	11.15	6.03
Do	11.24		11.18								
Do	[b d] 14.22	[b d] 13.96	[b d] 14.00	[b d] 13.78	96.05	94.30	97.86	[b d] 13.24	[b d] 12.99	[b d] 13.48	5.90
Do	[b d] 13.70		[b d] 13.56								
Lyons	12.05	12.01	11.97	11.92	[c] 97.99	[c] 99.19	99.70	11.68	11.82	11.88	6.70
Do	11.97		11.88								
Mallinckrodt Chemical Works	11.25	11.27	11.21	11.24	98.9	99.00	99.70	11.12	11.13	11.21	6.8
Do	11.29		11.27								
Ruddiman	10.82	10.85	10.72	10.75	97.02	97.07	100.00	10.43	10.43	10.75	.....
Do	10.89		10.78								
Do	10.40	10.42	10.34	10.54	.....	.....	.....	.....	.....	.....	.....
Do	10.45		10.74								
Smith	[b] 14.65	[b] 14.70	[b] 14.60	[b] 14.64	[98.54	98.6	98.7	[b] 14.43	[b] 14.43	[b] 14.45	6.0
Do	[b] 14.76		[b] 14.68		[97.92	97.94	98.0	[b] 14.34	[b] 14.34	[b] 14.35	6.05
Average	.....	11.38	.....	11.30	98.03	97.68	98.81	11.19	11.20	11.27	6.44
Maximum	12.05	12.01	11.97	11.92	99.51	99.19	100.00	11.68	11.82	11.88	7.00
Minimum	10.40	10.42	10.34	10.54	96.0	94.30	93.40	10.43	10.43	10.75	5.90
Difference	1.65	1.59	1.63	1.38	3.51	4.89	6.60	1.25	1.39	1.13	1.10

[a] Based on per cent of morphine weighed on watch glass.
[b] Not included in average, maximum, and minimum results.
[c] Results obtained by mixing morphine of both sets of duplicates.
[d] Used hardened filter paper, otherwise same as other set of duplicates.
[e] Acid standardized against morphine.

TABLE III.—*Cooperative work on determinations of morphine in opium, Method III, Stevens.*

Name.	Without correction.				Average.	With correction, factor 1.12.				Average.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Blome	11.20	11.17	11.29	11.32	11.24	12.32	12.29	12.41	12.44	12.36
Dohme	11.97	11.68	11.86	11.83	11.83	13.09	12.80	12.98	12.95	12.95
Doolittle	11.72	.....	.....	.....	11.72	12.84	.....	.....	.....	12.84
Havenhill	11.33	11.35	11.48	11.44	11.40	12.45	12.47	12.60	12.56	12.52
Kebler	11.52	11.67	*ab*11.47	*ab*10.95	11.60	12.64	12.79	*ab*12.59	*ab*12.07	12.71
Lyons *c*	*ad*12.00	*ad*12.14	*ab*11.82	.....	*a* 11.99	*ad*13.12	*ad*13.26	*ab*12.94	.....	*a* 13.11
Mallinekrodt Chemical Works	11.01	11.14	.....	.....	11.07	12.13	12.26	.....	.....	12.19
Puckner	11.36	11.53	11.22	11.25	11.34	12.48	12.65	12.34	12.37	12.46
Ruddiman	11.27	11.20	.....	.....	11.23	12.39	12.32	.....	.....	12.35
Smith	*a* 12.93	*a* 12.85	*a* 12.81	.....	*a* 12.89	*a* 14.05	*a* 13.97	*a* 13.93	.....	*a* 14.01
Average	11.42	11.39	11.46	11.46	11.43	12.54	12.51	12.58	12.58	12.55
Maximum	11.97	11.68	11.86	11.83	11.83	13.09	12.80	12.98	12.95	12.95
Minimum	11.01	11.14	11.22	11.25	11.07	12.13	12.26	12.34	12.37	12.19
Difference	.96	.54	.64	.58	.76	.96	.54	.64	.58	.76

a Not included in average, maximum, and minimum results.
b Per cent by weight.
c Acid standardized against morphine.
d Stood thirty-six hours before morphine was separated.

TABLE IV.—*Summary of results of cooperative work on opium by Methods I, II, and III.*

Method.	Amount of morphine on filter paper.	Amount of morphine on watch glass.	Purity by acid titration.	Purity by KOH, or Lyons's method.	Purity by lime water.	Morphine in opium by acid titration.	Morphine in opium by KOH, or Lyons's method.	Morphine in opium by lime water.	Moisture at 110° C.
	Per cent.	*Per cent.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
I, average	13.85	13.74	96.99	93.22	93.04	13.31	12.68	12.70	6.62
II, average with correction, *a* 1.105	12.485	12.405	98.03	97.68	98.81	12.295	12.305	12.375	6.44
III, average with correction, 1.12	*b* 12.33	.....	.....	.....	*b* 99.86	12.55	.....	.....	.....
II, average without correction	11.38	11.30	98.03	97.68	98.81	11.19	11.20	11.27	6.44
III, average without correction	*b* 11.21	.....	.....	.....	*b* 99.86	11.43	.....	.....	.....
I, difference between highest and lowest included in average	1.07	1.40	4.23	10.08	10.31	1.96	1.15	1.21	1.60
II, difference between highest and lowest included in average	1.65	1.63	3.51	4.89	6.60	1.25	1.39	1.13	1.10
III, difference between highest and lowest included in average	*b*. 52	.....	.....	.....	.....	.76	.....	.....	.....

a This applies to the per cent of morphine only.
b Based on morphine obtained gravimetrically.

The results obtained by volumetric solutions have all been calculated to the molecular weight of the 1890 Pharmacopœia, except in the case of Stevens's method, which it was deemed best not to change. It is very desirable to use uniformly, molecular weights based on the same system, and it was the referee's intention that the Pharmacopœia should be used as the basis of all of the work, but even though this has not been carried out completely the variations from this cause are very small compared with the great differences due to manipulation or inherent defects of the methods. The criticism has been made that a greater or smaller amount of the morphine present in opium is retained in the solvents employed for analysis and therefore not accounted for, and if a correction is added in one method a suitable correction should be added to all other methods for comparison.

The object of this work was, first, to determine to what extent the results of the various chemists agreed when working with the same method and material, and, second, to ascertain to what extent the results of the several methods, as used at present, agree in the hands of the same worker. Some consider it necessary to standardize the acid used for titration against the alkaloid to be titrated. The referee, however, dissents from this view on the ground that such a procedure would introduce unnecessary details without in any way insuring greater accuracy. Alkaloids themselves do not represent a higher degree of purity than do the chemical reagents customarily employed in adjusting the strengths of volumetric solutions. The methods for determining alkaloids volumetrically ought not to require a system for preparing standard solutions which in any way differs from present methods, unless some good reason exists, which does not appear to be the case at present.

The results given are quite unsatisfactory, even when the high and low results of Smith and Doolittle are excluded. Two separate workers at most ought not to vary more than one-half per cent with the same method and material, and duplicate results of the same worker should not approximate this difference. (The per cent used in this connection is based on the per cent of actual morphine.) But the difference between the highest and the lowest results exceeds 5 per cent, which is remarkable, especially when it is noted that all of the workers are experienced analysts. Even after excluding the highest and lowest results and such as for any reason appear abnormal, though such figures at times obtain in practice even when the utmost vigilance is exercised, the differences between the maximum and minimum figures are from two to three times too great. Duplicates of the same workers in three cases vary 0.54, 0.68, and 1.07 per cent. Such differences are not flattering to the present status of opium assaying. It is quite possible that more attention to details will contribute to greater uniformity.

The average difference between the amount of morphine weighed on the filter papers and on the watch-glasses is nearly one-tenth of 1 per cent less on the watch-glasses—being 0.11 per cent by Method I, and 0.08 per cent by Method II. Some prefer to weigh the morphine on the filter papers, while others think it desirable to remove the morphine and weigh it separately. These results indicate that there is nothing gained in removing the morphine from the filters before weighing. In removing the morphine from the filter papers fibers of the filter are carried with the morphine, unless hardened filters are used, as advised by Ruddiman. The amount, of course, is small, but the solution resulting from titration of the morphine sometimes looks as if a considerable quantity were present. At times, the morphine becomes electrified and very difficult to manage. To obviate this difficulty Puckner has been satisfactorily using gooch crucibles provided with paper disks instead of asbestos, as is done in other work.

The degree of purity of the morphine obtained by Method I is higher by acid titration than by the other two correction methods. Lyon's method and the lime-water method indicate a higher degree of contamination, and the results, while not so uniform as is desirable, run somewhat parallel. There is no doubt, however, that,

judging from certain colored solutions alone, lime-water dissolves nonalkaloidal matter, which is finally calculated as morphine. The results obtained by the three correction methods with the morphine produced by Method II are in better agreement than those produced by Method I, showing that the former method yields morphine of a higher degree of purity. Several years ago the referee advocated acid titration as a ready means for determining the purity of morphine, but an extended experience showed that while it was applicable for morphine obtained from many opiums, it was valueless for that derived from others, and it was impossible to tell in advance whether it would or would not work with a given sample of opium. The disturbing factor or factors have not been definitely determined.

In commenting on the methods for opium assaying in this cooperative work Mr. E. Mallinckrodt, jr., says:

The United States Pharmacopœia assay gives an alkaloid containing as much as 15 per cent of foreign matter in certain grades of opium. The titration, with either of these two indicators (litmus and cochineal), of the morphine obtained by the United States Pharmacopœia (1890) assay is useless for the following reasons: According to our experience precipitated morphine contains from 5 to 15 per cent of calcium ammonium meconate ($CaNH_4C_7HO_7, 3H_2O\pm$). As this salt contains three equivalents of base it must be alkaline to these indicators. In fact it titrates with cochineal in the pure state, consuming nearly as much sulphuric acid as morphine itself.

The conditions that prevail in the 1890 pharmacopœial assay process are excellent for the formation of calcium ammonium meconate. There seems to be very little doubt that the methods now used for arriving at the purity of the morphine are not entirely satisfactory; the lime-water process, however, seems to be the best for the present.

The argument is at times presented that the amount of impurity present in the morphine obtained by the 1890 pharmacopœial process is approximately equal to the morphine lost in the method of assay and therefore a correction is unnecessary. It is undoubtedly true that this condition frequently obtains, but it has never been satisfactorily proved that such is the case, and experienced operators believe that the foreign material contained in morphine obtained from certain kinds of opium far exceeds the amount of morphine lost by the process. There is at present no method available for ascertaining accurately the amount of morphine lost in the analysis, neither do we know of a process by which the precise quantity of impurities associated with the morphine can be determined. Even if we possessed such a method it would be unwise to assume that a relation of the above character exists until it has been definitely shown to be the case with the opium at hand.

The Pharmacopœia directs that the complete crystallization of the morphine should be accomplished in a "moderately cool place." It is seldom that any notice is taken of the temperature. The room temperature, which is frequently far from moderately cool, usually obtains. There is probably little doubt that the varying temperatures at which crystallization is effected contribute to the discrepancy. The variable amount of ammonia present also exerts an influence on the amount of morphine crystallized out. The directions specify the use of 10 per cent ammonia water, but if this article is made by diluting the 28 per cent strength usually supplied, without testing it, a material variation from this strength will probably be found, as the product is not generally true to label.

One great objection to the present pharmacopœial method is its consumption of time, yet manufacturers at times prefer even to extend the time, if by doing so satisfactory results can be obtained. Mallinckrodt's method, referred to in footnote *f*, Table I, is that of the United States Pharmacopœia, 1890, modified by Lamar[a] and the morphine reassayed by the pharmacopœial method. Lamar's modification consists in adding 60 instead of 10 grams of alcohol to the 20 grams of aqueous extract,

[a] Am. J. Pharm., 1900, *71*:36.

which precipitates certain foreign materials. The mixture is then filtered, and the residue washed with a mixture of alcohol and water, of the same strength, until the filtrate is free from bitterness, then 35 cc of water are added, the mixture evaporated to 14 grams, and the determination finished as directed by the original method.

The per cent of water of crystallization and possibly mechanically retained water in the morphine as given by the various workers seems to be within the limits of error, but slightly exceeds the one molecule customarily considered to be present. Theoretically, crystallized morphine contains 5.85 per cent of water of crystallization, while the average loss at 110° C by Method I is 6.62, and the loss by Method II is 6.44 per cent.

According to Blome's results on Method I, the element of time of crystallization is a very important factor, which has often been noted, and this emphasizes the necessity of adhering closely to prescribed details. Smith's results for all methods are abnormally high, but it should be observed that the results on the purity of the morphine are very good. Kebler's second set of duplicates for Method II, where hardened filter papers were used, are also unusually high. In this case filtration proceeded very slowly, and skins appeared to form on the surface. It was at first thought that the skins resulted from the formation of calcium carbonate, and while the morphine did contain a small amount of ash, it was not enough to warrant the conclusion that there was any calcium carbonate found during the process of filtration. It is difficult to explain the high results obtained in these duplicates.

It has been recommended that the per cent of inorganic matter in crystallized morphine forms a basis of correction, but thus far the results have not been satisfactory. Kebler obtained the following results in per cent from the morphine crystallized in the above work: Method I, 1.80 and 2.01; Method II, unweighable and 0.3; Method III, unweighable.

The above results do not represent a sufficient number of observations nor are they concordant enough to justify any conclusions, and different chemists may put varying constructions on the results. A brief summary, however, may be of service.

(1) Method I gives the highest per cent of pure morphine obtained by any of the corrections. (2) Method III gives the most concordant results in the hands of different chemists. (3) There does not seem to be any advantage in removing the morphine from the filter paper prior to the weighing, especially when the purity of the morphine is determined and the highest percentage is a desideratum. The objections to its removal are the electrifying of the morphine and contamination with the fibers of the filter. (4) The use of hardened filter papers and gooch crucibles provided with paper disks deserves study. (5) None of the methods used at present for determining the purity of the morphine is generally satisfactory. (6) It is desirable to determine the amount of calcium ammonium meconate formed by the present pharmacopœial method. (7) An examination of Lamar's modification of the present United States Pharmacopœia method may provide a remedy for some difficulties.

The work will be continued, and it is hoped that a greater number of chemists will assist.

SECOND DAY.

TUESDAY—MORNING SESSION.

The acting president called the meeting to order at 10 o'clock, and, after some instructions to the committees on recommendations, called for the report of the referee on ash, which was given as follows:

REPORT ON ASH.

By R. W. Thatcher, *Referee.*

The work of the referee on ash for this year has been confined to a continuation of the study of methods for determining sulphur in plant tissues. This study has occupied the attention of the referee on this subject for the past 2 years, but the results so far obtained have not led to definite conclusions. Previous to this year the investigation of methods for determining sulphur in organic combinations had been limited to sulphur in albuminoid form, and no attempt was made to ascertain whether the results obtained really included all the sulphur originally present in the plant tissue, the work being confined to a comparison of results obtained by different methods. It was deemed advisable, therefore, in planning the work for this year, to include samples for analysis which should contain sulphur in other than albuminoid form, and, if possible, to have at least one sample in which the true sulphur content was known. With a view to obtaining a pure product in which the theoretical percentage of sulphur could be calculated, correspondence was opened with the laboratory of a firm engaged in the manufacture of these products. In the course of correspondence the following statement concerning "artificial oil of mustard," or allyl thiocyanate, was received:

Although artificial oil of mustard is a very pure body which, when freshly prepared, has an almost definite boiling point, yet it can not, just as it is, be recommended as an original substance, since, like many organic sulphur compounds, it has a tendency toward polymerization. It could only be applied to the purpose intended if it were freshly distilled shortly before use.

This product was therefore decided upon as being suitable for the desired purpose, and a quantity of the freshly distilled oil was obtained for use in the cooperative work for this year. The percentage of sulphur in this oil being so high and its irritant fumes so strong, it was deemed wise to dilute it considerably before sending out samples to cooperating chemists. A mixture of approximately 10 parts of neutral olive oil (containing no sulphur) and 1 part of the allyl thiocyanate was prepared, the exact proportions taken being such that the resulting mixture contained 2.85 per cent of sulphur, equivalent to 7.125 per cent of sulphur trioxid.

In the meantime the secretary of the association had forwarded to the referee the names and addresses of chemists who had expressed to him their interest in the work on ash. Letters were sent to each of these chemists inviting their cooperation. Favorable replies were received from six. Four replied that it was impossible to undertake the work this year, and seven did not reply at all. Three of the chemists to whom the samples were sent have reported results on a part of the work outlined. The remainder of the analytical data reported below was obtained in the laboratory

of the State chemist of Washington and of the Washington experiment station. The following is a report of the cooperative work for this year:

DIRECTIONS FOR WORK.

The objects of the work on ash this year are twofold—first, to continue the study of the comparative value of the nitric-acid method and the peroxid method for the determination of total sulphur in organic materials, as directed by the association at its last meeting; and, second, to ascertain whether these methods are accurate and satisfactory for substances in which the sulphur is present in other than albuminoid form.

The samples for the work consist of (1) alfalfa hay, (2) cotton-seed meal, (3) white mustard, and (4) a mixture of neutral olive oil and Merck's artificial oil of mustard, containing a known amount of sulphur in the form of allyl isothiocyanate.

These samples have been thoroughly mixed and are ready for analysis. Determine moisture in the first three samples, preferably by drying in hydrogen, and report results. Report results of sulphur determinations in per cent of SO_3 on samples as received and on dry matter. Please report the results of your work not later than August 20, and make such criticisms of the method as your experience would suggest.

Apply the following methods to each of the four samples, making at least duplicate determinations in each case.

Method I.—Place 5 grams material in a $2\frac{1}{2}$ or 3 inch porcelain evaporating dish, add 20 cc concentrate nitric acid, and heat cautiously on a water bath until all danger of overflowing has passed. Then evaporate almost to dryness, add 10 cc of a 5 per cent solution of potassium nitrate, evaporate to complete dryness, and ignite, at first gently, then vigorously, until the residue is white. Dissolve this residue in hydrochloric acid and evaporate to dryness, and heat for some time in an air bath to render silica insoluble. Take up in water containing a little hydrochloric acid, filter to 150 cc or more, and precipitate the sulphuric acid with a solution containing 1 gram of barium chlorid, and complete the determination in the usual way. Make a blank test with the reagents. If time permits try the following modification in order to hasten the destruction of the organic matter: After adding the potassium nitrate and burning for some time, allow the dish to cool, add a few cubic centimeters of nitric acid, dry rapidly, and ignite cautiously to a white ash.

Method II.—Weigh out 15 grams of sodium peroxid and introduce most of it at once into a nickel crucible; convert into hydroxid by adding a little water and boiling, preferably over an alcohol lamp, until excess of water is completely driven off. Allow the hydroxid to cool until pasty and stir 2 grams of material into it as quickly as possible; heat cautiously until danger of foaming has passed, adding the remainder of the peroxid in small portions from time to time to complete the oxidation. The fused mass, after cooling, is to be dissolved in water, an excess of hydrochloric acid added, evaporated to dryness, and heated in an air bath to render silica insoluble. Take up the residue in water containing a little hydrochloric acid, filter and wash to about 400 cc and precipitate the sulphuric acid as before. Make a blank test with the reagents.

DETERMINATIONS OF MOISTURE.

The results of the determinations of moisture in the samples, as reported by the different analysts, are reported in Table I as a matter of record.

TABLE I.—*Moisture in samples.*

Analyst.	Alfalfa hay.	Cotton-seed meal.	White mustard.
	Per cent.	*Per cent.*	*Per cent.*
J. H. Gibboney, Blacksburg, Va	[a]8.09	6.75	7.91
F. T. Shutt, Ottawa, Canada	[b]7.18	5.29	6.24
A. T. Charron, Ottawa, Canada	[b]7.33	5.25	6.59
F. F. Flanders, Pullman, Wash	[b]5.77	5.51	6.50
	5.91	5.46	6.49
W. R. Bloor, Pullman, Wash	[a]7.66	6.68	7.34
R. W. Thatcher, Pullman, Wash	[a]7.84	6.87	7.87

[a] Dried in hydrogen in Caldwell tubes. [b] Dried in boiling-water oven on watch glasses.

Determinations of Sulphur.

The results of the determinations of sulphur by the cooperating chemists are reported in Table II. The percentages reported are calculated on the basis of moisture-free material, except in the case of the mixed oils, on which no moisture determinations were made.

Table II.—*Determinations of sulphur.*

[Results calculated to water-free basis.]

Analyst.	Percentage of sulphur (SO_3) found.							
	Alfalfa hay.		Cotton-seed meal.		White mustard.		Mixed oils.	
	Method I.	Method II.	Method I.	Method II.	Method I.	Method II.	Method I.	Method II.
J. H. Gibboney, Blacksburg, Va	0.306	.....	1.185	.....	[a] 2.568	.....	3.160	.....
	.304	.....	1.163	.....	[a] 2.564	.....	3.180	.....
F. T. Shutt, Ottawa, Canada	.327	.....	1.003	.....	4.047	.....	3.390	.....
A. T. Charron, Ottawa, Canada	.314	.....	1.070	.....	4.290	.....	.....	.....
F. F. Flanders, Pullman, Wash	.278	0.384	1.058	1.509	4.260	5.087	4.365	6.570
	.272	.398	1.096	1.369	4.355	4.957	4.455	6.050
W. R. Bloor, Pullman, Wash	.332	.372	1.372	1.449	4.364	4.918	3.715	5.362
	.324	.350	1.360	1.383	4.250	4.859	4.224	3.718
	.....	.....	.....	.....	.....	.....	3.454	4.393
	.....	.....	.....	.....	.....	.....	.....	5.716
R. W. Thatcher, Pullman, Wash	.292	.336	1.170	1.404	3.961	4.832	3.688	4.930
	.279	.332	1.172	1.410	3.928	4.850	3.478	3.728
O. M. Shedd, Lexington, Ky [b]	.319	.....	1.143	.....	3.750	.....	3.690	.....
	.302	.....	1.170	.....	3.572	.....	3.220	.....
Average	.303	.362	1.165	1.421	4.182	4.950	3.711	5.058

[a] Omitted from average. [b] Results received too late to be included in averages.

Comments of Analysts.

F. T. Shutt.—With one or two exceptions the data sent are from closely concordant duplicate results. The ignitions were finished in the muffle furnace.

F. F. Flanders.—The use of nitric acid in Method I, as suggested, materially shortens the time necessary to produce a white ash. The peroxid method is shorter in point of time required to produce ash, but the large quantity of sodium chlorid present interferes with the precipitation of barium sulphate. It is necessary that the solutions stand some time after addition of barium chlorid, or results will be low. (Mine stood over night.) In my judgment neither of these methods will give the true amount of sulphur in all kinds of organic substances, although the peroxid comes nearer the true amount than the Fraps method.

W. R. Bloor.—The peroxid method in all cases gave a higher percentage of sulphur than the nitric-acid method. As to ease of operation and time required the peroxid method has the advantage, requiring no more skill in operation nor more attention than the nitric-acid method, while taking very much less time, especially if the oxidation in the Fraps method is not hastened toward the end by the addition of nitric acid as suggested. Neither method appears reliable for the determination of sulphur in the mustard oil, and hence also probably not for any easily volatile substance, because the necessary heat drives off some of the material.

O. M. Shedd.—Only Method I was tried, modified, as suggested, by treating the partly burned residue with nitric acid, drying, and burning again. Without this treatment it would have taken a long time to burn the residue white. The 3-inch

dishes were found rather small for the first treatment with nitric acid, so we substituted 4-inch R. B. porcelain dishes in most of the work. Independent duplicates were carried out on each sample. A blank determination was made with the same amount of reagents as used in the determinations, and gave 0.0023 gram of barium sulphate. This amount was subtracted from the several weights of barium sulphate obtained in each experiment before calculating the per cent of sulphur.

R. W. Thatcher.—This year's experience has entirely overcome my prejudice against the peroxid method. My present supply of sodium peroxid is entirely free of sulphur, and the small loss by sputtering when water was first added to it was consequently of no importance. By boiling the sodium hydrate until excess of water was completely expelled, no difficulty from frothing when the organic material was added was experienced. Nickel always appears in the filtrate, but does not interfere with the determination of sulphuric acid. The large amount of salt present retards precipitation of barium sulphate, especially if only a small amount of the latter is present. Complete separation was obtained by allowing precipitates to stand over night, however. In the duplicate determinations by the nitric-acid method one sample was ashed without addition of extra nitric acid and the other by the suggested modification of Fraps process. The amount of sulphur obtained was in each case identical, the procedure being much shortened by the use of the additional nitric acid. Results by this method were invariably lower than those obtained by the peroxid method.

Remarks.

The results of the cooperative work this year clearly show that the peroxid method gives higher results than does the nitric-acid method. So far as the referee can learn no modification of the latter method has yet been devised which will cause it to yield higher results, or, in other words, to include more of the sulphur originally present in the plant tissue.

It is still a question whether the peroxid method gives results which really include all the organic sulphur in the material to be analyzed. The results obtained on the sample of oils in which the sulphur content was known were very widely scattering and in every case were too low. The sample which contained sulphur equivalent to 7.125 per cent SO_3 gave figures varying from 3.160 per cent to 4.455 per cent, with an average of 3.711 per cent, by the nitric-acid method, and 3.718 per cent to 6.57 per cent, average, 5.058 per cent, by the peroxid method. It is probable that the selection of a test substance which volatilizes as easily as does allyl thiocyanate was unfortunate.

There has recently appeared an article by W. E. Barlow on "The losses of sulphur in charring and in ashing plant substances, and on the accurate determination of sulphur in organic substances,"[a] in which the author describes a method devised at the University of Göttingen, under the direction of Prof. B. Tollens, for the combustion of plant substances in a closed tube in an atmosphere of oxygen in such a manner that all the sulphur is completely oxidized and is later absorbed in a column of sodium carbonate. According to the author this method is an "absolute" one, giving a true determination of total sulphur in plant substances. The author also compared results by his method with those obtained by the Fraps nitric acid method and in a single case with those from the peroxid method. Results by the Tollens-Barlow method were always higher than by the Fraps method. The author then carried out the nitric-acid oxidation in a closed apparatus in such a manner that the escaping fumes could be collected and analyzed, and showed where the losses of sulphur occur. He demonstrated that with plant substances like corn, oats, and mustard seed there is a loss of sulphur in the Fraps process corresponding to from 12.7 per cent to 14.2 per cent of the total sulphur present.

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[a] J. Am. Chem. Soc., 1904, *26:* 341.

The averages of the results obtained by the cooperating chemists this year show that the loss of sulphur by the Fraps process, as determined by the difference between the results from this method and those from the peroxid method, is from 15.7 per cent to 18 per cent. The similarity of these figures to those just quoted suggests that the peroxid method probably gives correct values for total sulphur in plant substances like those used this year and that the low results obtained on the sample of oils was due to the extreme volatility of the allyl thiocyanate under the working conditions of the method.

The referee had hoped to investigate the Tollens-Barlow method with a view of reporting upon its possible adaptability as an official method, but was prevented by press of other work from doing so.

RECOMMENDATIONS.

The results reported above show that the peroxid method always gives higher results than the nitric-acid method, but that neither method gives results which even approximate the total amount of sulphur in the sample in which the true sulphur content was known. Therefore the referee recommends:

(1) That the study of the nitric-acid and peroxid methods be continued next year.

(2) That the referee on ash for next year be requested to make determinations of the total sulphur in the samples used for cooperative work by the Tollens-Barlow or "absolute" method for sulphur in organic combinations.

Mr. FRAPS. At least it may be said that there has been some advance made over the methods of two or three years ago, when only one-fifth or even less of the sulphur was estimated. All of the methods are yet in a formative condition, and none of them is worthy of being adopted even provisionally by the association.

Mr. WILEY. The difficulties of estimating sulphur by any ordinary method of incineration have long been known. The question has arisen as to whether sulphur should be considered as a part of ash. The necessity of determining the total amount of sulphur in a plant substance is certainly very great. Agricultural chemists should give special attention to two considerations: First, What is ash? Second, How are those constituents, such as sulphur and phosphorus, which exist in organic combination to be distinguished from the sulphur and phosphorus which exist in inorganic combination and are properly parts of the ash? A large field is open for research work on this point which should be carefully cultivated. It is suggested that these materials may be burned in a closed chamber. They have been burned in bomb calorimeters, and probably some such method will be adopted.

Mr. THATCHER. I think it was recommended by Mr. Fraps, when referee, that the title of this section of the work be changed to read: "The determination of inorganic plant constituents." I would have been inclined to recommend such a change this year but thought that it had not been favorably received heretofore. I wish to say further that I have repeatedly analyzed Washington soils which by the official method of solution in hydrochloric acid showed not the slightest trace of sulphur, and yet these soils produce large yields of crops which contain highly albuminous substances. I am under the impression

that in the State of Washington some form of sulphur will be recognized as a fertilizer. The subject needs further investigation.

Mr. Fraps. A recommendation in regard to the change of the name of the work on ash, mentioned by Mr. Thatcher, has, I think, already been adopted.[a]

Mr. Wiley. In regard to the apparent lack of sulphur in the soils of Washington State, I would say that the sulphur may exist in a form which is not soluble in hydrochloric acid, or it may be in an organic form which becomes oxidized. Sulphur must certainly be present.

Mr. Wheeler. There is a great deal of confusion as to what is meant by plant food, and even in two books by the same author we sometimes find the term used with different meanings. I think that the chemist and the botanist should collaborate and discuss the term "plant food" for the purpose of defining it. I move that a committee of five be appointed from this association to act in the matter and that an invitation be extended to the botanical section of the American Association for the Advancement of Science to appoint a similar committee of five to cooperate with the committee from this association in defining plant food.

Mr. Van Slyke. I do not wish to be understood as objecting to this motion, but it seems to me that problem is a great deal more complicated than the question of a line of demarcation between plant and animal life. We are confronted by almost an infinite number of exceptions, and while desiring to systematize what is now in a chaotic condition we must not be too hopeful of drawing a rigid line of demarcation.

Mr. Wiley. It does not seem that because a problem is difficult we should refrain from attempting to solve it. The very condition of affairs which Mr. Wheeler has mentioned shows the great necessity for a conference.

The motion was passed, and the president named the following committee:

H. W. Wiley, chairman; H. J. Wheeler, L. L. Van Slyke, E. W. Magruder, and B. W. Kilgore.

The report of Mr. Kebler as chairman of the special committee on the testing of chemical reagents was then called for, this committee having been appointed to cooperate with a similar committee of the American Chemical Society, already at work.

[a] Note by the editor.—The change referred to—i. e., the substitution of the title "Determination of inorganic plant constituents" for that of "Ash"—was made by action of the association at the eighteenth annual meeting (see Bureau of Chemistry Bulletin No. 67, page 150), and the work is so referred to in the list of referees for 1904–5.

REPORT OF THE COMMITTEE ON THE TESTING OF CHEMICAL REAGENTS.

By L. F. Kebler, *Chairman.*

A thorough knowledge of the quality of the chemical reagents used by the analyst ought certainly to be the first desideratum in his work. Without such a knowledge it is difficult to understand how chemists can expect to obtain concordant or reliable results, for it has been known for a number of years by those who have even casually interested themselves in this subject that the chemicals supplied for analytical work are frequently of a very questionable character. The very existence of this committee points to this fact. Some chemists have adopted the commendable practice of purifying all chemicals used in careful scientific investigations. It is probably seldom necessary to resort to this expedient for analytical work, but the careful analyst undoubtedly should examine his chemicals before using them.

It is customary usually to order chemical reagents by the designation C. P., meaning chemically pure, and dealers have fallen into the practice of delivering them marked to suit the order of the chemist. Undoubtedly the reader, in common with certain members of the committee, left his alma mater under the impression that the labels on the packages of the chemicals he has been using tell the whole truth and nothing but the truth. The designation C. P. should mean chemicals of a high degree of purity. It is frequently not necessary to investigate very far, however, before it is found that the labels misrepresent the existing condition, and that the term "C. P." is without meaning, being frequently used as a convenience. For example, it is customary for dealers to label inorganic acids, glycerin, etc., of fairly high grades C. P., it being known to them that they are not strictly chemically pure in quality. The trade has brought into usage this meaning of the designation, and consumers generally order certain commercial grades of chemicals for use in the arts by this abbreviation. These products are usually satisfactory for qualitative work and manufacturing purposes, but they ought not to masquerade as being of the highest degree of purity. Such a custom works detriment to articles that are of the best quality, and naturally drives them out of the market to a considerable extent.

All who have made atomic weight determinations know how difficult a task it is to make chemicals absolutely 100 per cent pure. It would therefore seem that such a degree of purity would be too exacting. Many of us know very well that it is seldom possible to obtain as high a degree of purity on a commercial scale, where the ultimate cost is a ruling factor, as in scientific investigations, where neither time nor cost is considered. Within recent years the very desirable practice of labeling chemicals free from certain impurities has come forward. This at first thought appears to be a step in the right direction. For most chemical operations the presence of certain impurities is not objectionable, yet it is desirable to remove all foreign matter as thoroughly as practicable, even at a slight increase in cost, because chemists are frequently called on to use the same reagent for different operations, and if the system is carried too far each laboratory will be compelled to carry in stock several grades of the same reagent, which would involve an unnecessary expense, increase the chemist's duties, and be liable to lead to numerous difficulties. Commendable as appears to be the system of labeling chemicals free from certain impurities, it is unfortunate that manufacturers and dealers even in this are not always showing good faith. For example, potassium permanganate and magnesium oxid C. P. marked "free from sulphur" contained this impurity; copper sulphate marked "C. P., absolutely free from iron" was not true to label; sodium hydroxid delivered as free from sulphur, nitrogen, and aluminum, was contaminated with these bodies. If dealers do business of such a character the system of indicating the presence of certain impurities will be destroyed by its own inadequacy.

Differences in qualitative and quantitative analyses are undoubtedly often traceable to impurities in chemical reagents. It is probably seldom thought that the source of discordant results is in the chemical reagents used. Many analysts seem to be satisfied with the belief that they are using the purest reagents obtainable. It is true very pure chemicals are obtainable, if insisted on, but as has been pointed out the various terms expressing purity are very elastic, having different interpretations in different establishments. What will be considered pure in one factory is entirely different from the product prepared by another firm and marked exactly the same. A recognized uniform degree of purity for the same grade of chemical would undoubtedly be as welcome to the manufacturers as to the chemist, and the best manufacturers and dealers appear to be anxious to have chemists set standards for chemical reagents. They realize that it would place competition on a fair, equitable basis, which is all that honest dealers demand. They are anxious to supply the quality of reagents called for, if fair prices are forthcoming and they are not compelled to compete with inferior articles.

The committee recognized the necessity of restricting the work for the past year to a few chemicals. With this end in view instructions for testing 12 chemicals were sent out to about 400 chemists inviting their cooperation in the work. To these invitations 10 chemists responded favorably, indicating that they would be willing to do more or less of the work outlined. When the time came for the reports to be in the chairman's hands, all who had expressed a willingness to assist were informed that their results should be sent in as soon as possible. Of the 10 chemists who had responded, 2 sent in reports. The committee is very grateful to those who assisted, but it is surprising to find such great apathy in regard to this important work.

The committee planned the work in such a way that if chemists investigated their reagents it would involve only a small amount of work to collect the results and forward them to the chairman. It is hoped that chemists will bear this work in mind for future reports.

For the present report the following instructions were sent out:

THE TESTING OF CHEMICAL REAGENTS, A. O. A. C. COOPERATIVE WORK, 1904.

At the recent meeting of the Association of Official Agricultural Chemists a committee was appointed to cooperate with a similar committee of the American Chemical Society in an investigation of the quality of chemicals used for analytical purposes. The A. O. A. C. committee desires the assistance of every chemist of the association and such other chemists as are willing to take a part in the work. The committee invites suggestions as to what chemicals should be included in this work, the degree of purity required, and the nomenclature to be employed. Shall we retain the designations C. P., pure and commercial, or shall a new classification be made, and in either case what shall be the basis of standards?

Below will be found a list of 12 chemical reagents to be tested as received by chemists in original packages. The report should include the name of the manufacturer. The observations to be made are specified, and the following books are to be used, unless otherwise indicated: "Die Prüfung der Chemischen Reagentien," third edition, by C. Krauch, or a translation of the same; "The Testing of Chemical Reagents," by J. A. Williams and L. W. Dupré, published by D. Van Nostrand Company, 23 Murray street, New York, N. Y., and the 1890 United States Pharmacopœia (U. S. P.). In case two different tests are given for the same impurity, the one to be followed is specified.

Glacial acetic acid, 99.5 per cent.

Physical appearance; specific gravity at 20° C.; congealing point; per cent of acid by titration using phenolphthalein as indicator; miscibility in water and alcohol; nonvolatile matter in 50 cc on steam bath and also by subsequent ignition; presence of HCl, H_2SO_4 in 10 per cent solution and twelve hours standing; presence of salts of aluminum, copper, lead, calcium, and iron in 10 per cent solution. (Saturate a 10 per cent acid solution with ammonium hydroxid, 0.900, no change within twenty-four hours; to separate portions of alkaline solution add ammonium sulphid solution

and ammonium oxalate solution, no change should be manifest.) Presence of acetone, etc., by iodoform test in 10 per cent solution (Richter). Presence of H_2SO_3 and HCO_2H (U. S. P.); empyreuma, by $KMnO_4$ solution (Krauch); render alkaline with KOH solution and note odor (U. S. P.).

Dissolve 20 mg powdered $K_2Cr_2O_7$ in 10 cc conc. H_2SO_4, then add 10 cc of acetic acid and mix well. No green color should develop within one-half hour.

Test 90 per cent and lower strengths acetic acids by pharmacopœial requirements for acetic acid.

Hydrochloric acid.

Physical appearance; specific gravity at 20° C.; per cent of acid by titration, using phenolphthalein as indicator; miscibility in water; nonvolatile matter in 50 cc on steam bath and by ignition after evaporation; H_2SO_4 in 10 per cent solution and twelve hours standing; presence of metals, copper, iron, aluminum, calcium, and lead; presence of chlorin (Krauch), except in place of using starch solution add a few drops of carbon disulphid and shake; bromid and iodid, liberate bromin or iodin with chlorin water, add carbon disulphid and shake; H_2SO_3 (Krauch); arsenic by Marsh-Berzelius method, running one hour.

Nitric acid.

Physical appearance; specific gravity at 20° C.; per cent of acid by titration using phenolphthalein as indicator; miscibility in water; nonvolatile matter in 50 cc on steam bath and by ignition after evaporation; H_2SO_4 and HCl in 10 per cent solution and twelve hours standing; presence of copper, lead, calcium, and iron (U. S. P.); hyponitrous acid (Krauch); bromin and $HBrO_3$ and iodin and HIO_3 (U. S. P.); arsenic by Marsh-Berzelius method, running one hour.

Sulphuric acid.

Physical appearance; specific gravity at 20° C.; per cent of acid by titration with phenolphthalein as indicator; nonvolatile matter in 50 cc after evaporation and ignition; miscibility in 4 to 5 volumes of water and alcohol (95 per cent); HNO_2 and HNO_3 (U. S. P.); H_2SO_3, HNO_2 (U. S. P.); presence of copper, lead, and iron (U. S. P.), selenium (Krauch); halogens and ammonium compounds (Krauch); arsenic by Marsh-Berzelius method, running one hour.

Ammonium hydroxid.

Physical appearance; specific gravity at 20° C.; per cent of NH_3 by titration, using cochineal as indicator; miscibility in water; nonvolatile matter in 50 cc on steam bath and by ignition after evaporation; presence of chlorid and sulphate in 10 per cent solution and twelve hours standing; presence of metals, calcium, zinc, copper, and lead; carbonic acid; empyreumatic bodies; arsenic by Marsh-Berzelius method, running one hour.

Ethyl alcohol, about 95 per cent.

Physical appearance; specific gravity at 20° C.; miscibility in water; nonvolatile matter in 100 cc on steam bath and by ignition after evaporation; foreign odor like fusel oil (U. S. P.); aldehyde or tannin (U. S. P.); organic impurities by silver nitrate test (U. S. P.); furfurol (Krauch); reaction to litmus paper and the number of cubic centimeters of one-hundredth normal potassium hydrate solution required to neutralize the acidity of 100 cc of the alcohol, using phenolphthalein as indicator. Before titrating, dilute the alcohol with an equal volume of water, whose acidity to phenolphthalein has been determined. Deduct the acidity of the water from the total acidity of the mixture of alcohol and water, which gives the acidity of the alcohol.

Ethyl ether.

Physical appearance; specific gravity at 20° C.; miscibility in 95 per cent alcohol and in chloroform; boiling point; foreign odor; nonvolatile matter in 100 cc on steam bath; reaction to litmus; acidity to phenolphthalein in 100 cc. Determine as directed under alcohol. The water and the ether are not completely miscible, consequently it is best to make the titration in a glass-stoppered flask, shaking vigorously after each addition of one-hundredth normal potassium hydrate solution. Aldehyde, etc. (U. S. P.). Hydrogen peroxid and ozone (Krauch), the potassium iodid must be free from iodate and the liberation of free iodin is to be determined by a few drops of starch solution. Alcohol and water in excess (U. S. P.). The latter observation is to be made near 20° C. Water (Krauch).

Sodium and potassium hydroxid by alcohol.

Physical appearance; solubility in water and in 95 per cent alcohol; note color of alcoholic solution and change of color on standing of 10 per cent alcoholic solution. Per cent of alkali on titration, using phenolphthalein as indicator; presence of salts of calcium, iron, aluminum, and lead; chlorid, sulphate, nitrate, carbonate, and silicate (Krauch); presence of sodium compounds in potassium hydroxid by flame test and U. S. P.; ammonium compounds by Nessler's reagent in 10 per cent solution of alkali. Arsenic by Marsh-Berzelius method in 5 grams and one hour running. Test for the presence of phosphate by means of ammonium molybdate solution.

Sodium and potassium hydroxid.

(Commonly known as pure.)

Test according to U. S. P. requirements, but add test for arsenic by Marsh-Berzelius method and for the presence of phosphate by means of ammonium molybdate solution.

Potassium iodid.

Follow U. S. P. directions, except that a 10 per cent instead of a 5 per cent solution is to be used in applying the tests as specified, and in testing for sulphates the solution should be rendered acid with hydrochloric acid before the barium chlorid is added.

Those who will take part in the work are requested to inform the chairman of the committee to that effect as soon as possible, and to report results to him not later than August 1, 1904.

L. F. Kebler, *Chairman.*
A. L. Winton,
B. W. Kilgore,
Committee on the Testing of Chemical Reagents.

Washington, D. C., *March 15, 1904.*

To the above outline favorable responses were received from Mr. F. W. Woll of Madison, Wis., who sent the results of Messrs. G. A. Olson and A. Ystgard; Mr. Marckworth, of Columbus, Ohio, and the Bureau of Chemistry, represented by Messrs. George Hoover and L. F. Kebler. The following tables embody the results:

TABLE I.—*Acetic acid, glacial, 99.5 per cent.*

Observations.	Analysts.					
	Kebler.		Hoover.		Marckworth.	Woll.
Serial No	169	465	673	708		
Physical appearance	Good	Good	Good	Good	Good	Good.
Sp. gr. at 20° C	1.053	1.0511	1.052	1.052	1.054	1.0518.
Congealing point (°C.)	15° C	15.4° C	15.25° C	16° C	13° C	
Acid (per cent)	99.71	99.45	99	99.2	97.36 [b]	99.12.
Miscibility in water and alcohol	All proportions	All proportions	All proportions	All proportions	All proportions	All proportions.
Nonvolatile matter in 50 cc on steam bath.[a]	Not weighable	1.3 mg	0.5 mg	1.9 mg	0.9 mg	0.4 mg.
Inorganic acids	None	None	None	None	None	None.
Empyreumatic material	Trace	Not in excess	Trace	None	Within limit	Within limit.
Metals	None	None	None	None	None	None.
Reduction of potassium bichromate.	Green in 1 minute	Not within 2 hours	Green in 1 minute	None	Green color in 2 minutes.	None.
Acids reducing $AgNO_3$	None	None	None	None	None	None.
Acetone	Present	Present	None	None	Present	Absent.
Quality specified on label	Highest purity, 99.5 per cent.	Chemically pure, 99.5 per cent.	Highest purity, 99.5 per cent.	Not specified	Chemically pure, 99.5 per cent.	Not specified.

[a] No residue on ignition.

[b] This per cent based on specific gravity.

TABLE II.—*Ammonium hydroxid.*

Observations.	Analysts.		
	Hoover.		Woll.
Serial No	191	554	
Physical appearance	Good	Good	Good.
Sp. gr. at 20° C	0.922	0.9134	0.9254.
Nonvolatile matter in 50 cc	14.4 mg	2.2 mg	1.3 mg.
Residue on ignition	5.8 mg	2 mg	0.8 mg.
Acids	Trace of carbonic acid.	None	Trace of carbonic acid.
Metals	None	None	None.
Empyreumatic material	More than limit	Within limit	None.
Calcium	None	None	None.
Per cent ammonia.	20.55	23.64	20.50.
Quality specified on label	Specific gravity 0.925, reagent.	Strictly chemically pure. Sp. gr. 0.900.	Strictly chemically pure. Sp. gr. 0.90.

TABLE III.—*Ethyl alcohol, about 95 per cent.*

Observations.	Analysts.		
	Kebler.	Hoover.	Woll.
Serial No	38	679	
Physical appearance	Good [a]	Good [b]	Good. [a]
Sp. gr. at 20° C	0.8011	0.8099	0.8165.
Miscibility in water	All proportions	All proportions	All proportions.
Nonvolatile matter in 100 cc on steam bath	Brownish unweighable residue.	None	1.5 mg.
Fusel oil, aldehyde, and tannin	Much aldehyde	None	Traces of aldehyde.
Organic impurities	Much	None	Trace.
Furfurol	Much	None	Trace.
Reaction to litmus	Neutral	Neutral	Neutral.
Acidity to phenolphthalein		100 cc required 3.9 cc N/100 KOH.	100 cc required 1.6 cc N/100 NaOH.

[a] Delivered in barrels.

[b] Delivered in tin cans.

TABLE IV.—*Ethyl ether.*

Observations.	Analysts.					
	Kebler.			Hoover.	Woll.	
Serial No	273	310	384	640		
Physical appearance	Good	Good	Good	Good	Good [a]	Good. [a]
Sp. gr. at 20° C	0.714 (at 25° C.)	0.724 (at 15° C.)	0.717 (at 25° C.)	0.724	0.7135	0.718.
Miscibility in 95 per cent alcohol and chloroform.	All proportions	All proportions	All proportions	All proportions	All proportions	All proportions.
Boiling point (°C.)	33–39° C	34–41° C	34–36° C	35–40° C	32–40° C	33–39° C.
Foreign odor	Present	None	None	None	Disagreeable	Present.
Nonvolatile matter in 100 cc	None	None	None	None	22.5 mg	17 mg.
Residue on ignition on steam bath.	None	None	None	None	7 mg	4 mg.
Reaction to litmus	Neutral	Acid	Acid	Neutral	Neutral	Neutral.
Acidity in 100 cc of phenolphthalein.	100 cc required 2.3 cc N/100 KOH.	100 cc required 7 cc N/100 KOH.	Not determined	100 cc required 1.4 cc N/100 KOH.	100 cc required 6.75 cc N/100 KOH.	100 cc required 140 cc N/100 KOH.
Aldehyde, etc	None	Present	None	None	Present	None.
Hydrogen peroxid and ozone	None	Present	None	None	Present	Present.
Alcohol and water	Within limit	Within limit	Full limit	Within limit	Present [b]	Present. [b]
Quality specified on label	For anæsthesia	U. S. Pharmacopœia, 1890, for anæsthesia.	U. S. Pharmacopœia, 1890, for anæsthesia.	U. S. Pharmacopœia, 1890.	Distilled over sodium.	Distilled over sodium.

[a] Distilled over sodium.

[b] Water indicated by adding sodium and also copper sulphate.

TABLE V.—*Hydrochloric acid.*

Observations.	Analysts.		
	Hoover.		Woll.
Serial No	581	643	
Physical appearance	Good	Good	Good.
Sp. gr. at 20° C	1.177	1.181	1.1733.
Per cent acid	35.55	38.40	34.19. [a]
Miscibility in water	All proportions	All proportions	All proportions.
Nonvolatile matter in 50 cc on steam bath [b]	3.8 mg	0.5 mg	1 mg.
Foreign acids	None	None	None.
Metals	None	None	None.
Halogens	Trace of chlorin	None	Trace of chlorin.
Arsenic	None	None	None.
Quality specified on label	Strictly chemically pure. Sp. gr. 1.20.	Strictly chemically pure. Sp. gr. 1.20.	Strictly chemically pure. Sp. gr. 1.20.

[a] This per cent based on specific gravity.

[b] No residue on ignition.

TABLE VI.—*Nitric acid.*

Observations.	Analysts.		
	Kebler.	Hoover.	Woll.
Serial No	177	644	
Physical appearance	Good	Good	Good.
Sp. gr. at 20° C	1.289	1.417	1.4136.
Per cent acid	46.70	68.50	69.36. [a]
Miscibility in water	All proportions	All proportions	All proportions.
Nonvolatile matter in 50 cc on steam bath	2 mg	Not weighable [b]	2.4 mg.
Foreign acids	None	None	None.
Metals	Trace of iron	Trace of iron [c]	None.
Halogens	None	None	None.
Arsenic	None	None	None.
Quality specified on label	Reagent. Sp. gr. 1.30.	Strictly chemically pure. Sp. gr. 1.42.	Strictly chemically pure. Sp. gr. 1.42.

[a] This per cent based on specific gravity.

[b] Residue not weighable on ignition.

[c] Test for iron from the trace of residue.

TABLE VII.—*Potassium hydroxid, by alcohol.*

Observations.	Analysts.				
	Kebler.		Hoover.		Woll.
Serial number	220	314	650	661	
Physical appearance	White sticks	Yellowish sticks	White sticks	White sticks	Not indicated.
Color of 10 per cent alcoholic solution	Clear	Dark and turbid	Clear	Colorless	Partially undissolved.
Per cent alkali	85.51	88.00	87.65	85.47	82.11.
Foreign metals	Aluminum	Trace of sodium	Aluminum	Aluminum	Trace of sodium.
Foreign salts except carbonate and silicate	Trace of chlorid	Chlorid and nitrate	Chlorid and sulphate.	Chlorid and sulphate.	Chlorid.
Solubility in water	Good	Good	Good	Good	Good.
Silicate	None	Present	None	None	Trace.
Carbonate	Within limit	Full limit	Full limit	Within limit	Present (amount not indicated).
Ammonium compounds	None	None	None	None	None.
Quality specified on label	Reagent, purified by alcohol.	Pure by alcohol	Pure by alcohol	Strictly chemically pure,[a] free from H_2SO_4.	Pure by alcohol.

[a] Method of purification not indicated.

TABLE VIII.—*Potassium hydroxid, pure.*

Observations.	Analysts.		
	Kebler.	Hoover.	Woll.
Serial number	221	596	
Physical appearance	White sticks	Good	Not indicated.
Per cent alkali	84.79	86.43	71.29.
Foreign metals	None	None	Trace of sodium.
Foreign salts except carbonate and silicate	Chlorid and sulphate.	Chlorid and sulphate.	Chlorid and sulphate.
Solubility in water	Good	Good	Good.
Silicate	None	None	Trace.
Carbonate	Within limit		Present (amount not indicated).
Quality specified on label	Purified, reagent	Pure lumps	Pure.

TABLE IX.—*Potassium iodid.*

Observations.	Analysts.							
	Kebler.					Hoover.		Woll.
Serial number	4	5	39	222	223	503	682	
Physical appearance	Fair	Poor	White crystals	White crystals	White crystals	White crystals	White crystals	Not indicated.
Solubility in water	Good	Good	Turbid	Good	Good	Good	Good	Do.
Salts insoluble in alcohol	None	None	Mechanical impurity.	None	None	None	None	Do.
Alkali in 1 gram	0.6 cc N/10 acid.	0.14 cc N/10 acid.	0.34 cc N/10 acid.	....do	Neutral	0.06 cc N/10 acid.	0.12 cc N/10 acid.	Do.
Foreign metals	Trace sodium	Sodium	None	....do	None	None	None	None.
Foreign salts except iodate	Sulphate and chlorid.	Chlorid	Chlorid and sulphate.	Trace of sulphate.	....do	Trace of sulphate.	....do	Do.
Iodate	Present	None	Present	None	....do	None	....do	Do.
CC N/10 $AgNO_3$ required per gram.	59.26	59.49	60.09	60.09	60.39	60.39	60.5	Not indicated.
Quality specified on label	Chemically pure crystals.	Not specified	Not specified	Reagent	Reagent (neutral).	Chemically pure crystals.	Chemically pure	Chemically pure.

TABLE X.—*Sodium hydroxid, by alcohol.*

Observations.	Analysts.						
	Kebler.				Hoover.		Woll.
Serial number	240	390	391	459	649		
Physical appearance	White sticks	White sticks	White sticks	White sticks	White sticks		Not indicated.
Solubility in water	Good	Good	Good	Good	Good		Good.
Color of 10 per cent alcoholic solution.	Yellow on standing	Turbid colorless solution.	Yellow on standing	Turbid colorless solution.	Clear		Turbid, partially insoluble.
Per cent alkali	95.22	93.29	97.03	98.34	98.21		95.20.
Foreign metals	Aluminum	Limit of aluminum	Trace of aluminum	Excess of aluminum	Trace of aluminium		None.
Foreign salts, except carbonate	Chlorid and sulphate.	Chlorid, sulphate, and silicate.	Chlorid and sulphate.	Chlorid, sulphate, and silicate.	Chlorid and sulphate.		Chlorid, sulphate, and silicate.
Ammonium compounds	None	None	None	None	None		None.
Carbonate	Excess	Excess	Within limit	Excess	Within limit		Present.[a]
Calcium	None	None	None	None	None		None.
Quality specified on label	Reagent, pure (purified by alcohol).	Pure by alcohol	Pure by alcohol	Reagent, pure (purified by alcohol).	Pure by alcohol		Pure by alcohol.

[a] Carbon dioxid in appreciable quantity.

TABLE XI.—*Sodium hydroxid, pure.*

Observations.	Analysts.		
	Kebler.	Hoover.	Woll.
Serial number	239	551	
Physical appearance	Creamy white sticks	White sticks	Not indicated.
Solubility in water	Some residue	Good	Not all soluble.
Per cent alkali	95.23	94.31	85.04.
Foreign metals	Excess of aluminum	Trace of aluminum	Aluminium, iron, potassium.
Foreign salts, except carbonate and silicate	Chlorid, 0.23 per cent; excess of sulphate.	Chlorid and sulphate.	Chlorid and sulphate.
Silicate	Present	Present	Present.
Carbonate	Excess	Within limit	Present (amount not indicated).
Quality specified on label	Purified, reagent	Purified sticks	Pure.

TABLE XII.—*Sulphuric acid.*

Observations.	Analysts.		
	Kebler.	Hoover.	Woll.
Serial number	251	646	
Physical appearance	Good	Good	Good.
Specific gravity at 20° C	1.837	1.836	1.8363.
Per cent acid	95.27	95.25	94.68.[a]
Nonvolatile matter in 50 cc on steam bath	Not determined	Residue not weighable.	6 mg.
Residue on ignition	do	do	4 mg.
Miscibility in water and 95 per cent alcohol	All proportions	All proportions	Slightly turbid in alcohol.
Foreign acids	None	None	None.
Metals	do	do	Trace of lead.
Halogens	do	do	None.
Ammonium compounds	do	do	Do.
Arsenic	do	do	Do.
Quality specified on label	Reagent, specific gravity 1.84.	Strictly chemically pure, specific gravity 1.84.	Strictly chemically pure, specific gravity 1.84.

[a] Per cent based on specific gravity.

From the limited number of results reported it is not permissible to draw any general conclusions nor to indicate standards, but a number of comments may be made.

Acetic Acid, Glacial, 99.5 Per Cent.

Considerable difficulty has been experienced by the Bureau of Chemistry in securing glacial acetic acid 99.5 per cent pure that would stand the rigid sulphuric acid, potassium bichromate test, and certain chemists and manufacturers have put themselves on record that it was impossible to prepare such an acid. The chairman of this committee, however, knew that the above statement needed modification, because the Bureau of Chemistry has not only received such acids, but they have actually been prepared in the laboratory, where a high-grade acid is necessary for certain oil work.

This report records results on three acids, obtained from two different sources, that stand this test, and other manufacturers believe they can supply it. What the impurity or impurities are has not been determined, but it is quite evident that the pure article will stand the sulphuric acid, potassium bichromate test. It should be said in this connection that, aside from the response to this test, most samples examined so far are of good quality and can be used for ordinary work, though the strength frequently drops below 99.5 per cent.

Ammonium Hydroxid.

The few results on ammonium hydroxid bring out several points. It will be noted that the specific gravity of the last two samples was marked 0.90, which corresponds to 28 per cent of ammonia gas, but the actual specific gravities were considerably above 0.90, and the amount of ammonia gas was correspondingly deficient. It is a very common occurrence to find that the specific gravity given on the labels of ammonium hydroxid containers is not in accord with the contents of the packages. There is no excuse for this condition in the case of small sealed packages, but when the chemical is handled in carboys, as is frequently necessary, and there is difficulty in sealing the packages, it is of common occurrence and is not easy to prevent, especially in warm weather.

The actual specific gravity of sample No. 191 agrees well with that given on the label, but the amount of ammonia is 25 per cent below the strength usually delivered for analytical work. This chemical frequently forms the basis of more dilute reagents, and it is possible that a weaker solution is better suited to the uses of the manufacturer, which point should be considered, and if such is the case a lower per cent should be adopted as the standard. Whatever is done the analytical reagents sold by manufacturers should be of known, uniform strength, unless the chemist specifies some special strength. The sample in question is of poor quality, containing a large amount of nonvolatile and empyreumatic material. It is possible that the source of contamination was a rubber stopple used to close the container. A number of cases have been found where the stopples and luting materials were the sources of contamination. Manufacturers undoubtedly will not permit careless packing or the use of cheap material, and thus run the risk of ruining what would otherwise be superior goods, if their attention is called to the subject.

Ethyl Alcohol.

Nothing on the labels indicated the quality of the article. The per cent of alcohol is very good. Barrel alcohol usually contains more foreign material than is compatible with the purity required of this reagent for analytical work and should always be distilled before using. The article delivered in tin cans, as far as examined, is of good quality.

Ethyl Ether.

One-half of the samples examined are of satisfactory quality. No. 310 is excessively acid and contains objectionable foreign bodies. Not much reliance can be placed on the action of ether on litmus paper as ordinarily applied. The two samples reported by Mr. Woll were marked as being distilled over metallic sodium, which would indicate products of superior quality. As a matter of fact, they are very inferior goods. One possessed a disagreeable odor and the other some foreign odor. Most ether when examined by evaporation on clean filter paper has a foreign odor of some kind. The amounts of nonvolatile residues on the steam bath and on ignition in 100 cc are unjustifiable, and such ethers are certainly not suitable for analytical work. The amount of acid in the last sample, indicated by the use of phenolphthalein, is surprising. Mr. Woll makes the following remarks on the first sample reported by him: "The nonvolatile matter was chiefly oil of some nature, which evidently had been used in the manufacture of composition cork. Composition corks in original packages of the same manufacturer's chemicals on treatment with pure redistilled ether supplied a large amount of this fat or oil, which possessed a sharp, penetrating odor. The amount of this oil in the ether was sufficiently large to introduce a perceptible error in the determination of the fat content of substances. The cork was a very fine granulated composition, giving an exceedingly large surface to the oil, which undoubtedly accounts for the large amount present in this ether."

Hydrochloric and Nitric Acids.

All samples examined were of the same brand. They are all of fair quality, but it should be observed that they are not uniformly of the same degree of purity. Several samples contain an excess of nonvolatile matter, and two of the samples of hydrochloric acid contain traces of chlorin.

Potassium Hydroxid by Alcohol.

The results given emphasize the necessity of testing this chemical before using it for careful work. No. 314 was very poor quality physically and imparted considerable color to an alcoholic solution, yet otherwise tested fairly well. Attention should be called to the manner of marking No. 661 and the fact that it contains sulphate. It seems difficult to prepare this chemical to contain 90 per cent of alkali.

Potassium Hydroxid, Pure.

It is generally understood that this grade of potassium hydroxid is not as good as the article prepared by the use of alcohol, but the above results are not in accord with this belief, excepting the low percentage of alkali contained in the sample reported by Mr. Woll.

Potassium Iodid.

The unsatisfactory quality of this chemical is frequently commented on, particularly in respect to alkalinity and the presence of iodates. It is the common belief that the coloration resulting when an aqueous solution is acidified with an inorganic acid is due to the presence of an iodate. Aqueous solutions of potassium iodid are frequently colored when acidulated, but a further examination will show that the coloration is not always due to the presence of free iodin, but to some unknown cause. It is a very difficult and expensive operation to make this chemical free from chlorids, but such is not the case with sulphates. Neutral potassium iodid can be manufactured at a slight increase in price, but it seems to be a well-established fact that such a product does not keep as well as an article containing a limited amount of free alkali, which is not objectionable for most analytical work.

The limit set by the United States Pharmacopœia is that 10 grams must not require more than 0.5 cc of decinormal acid to neutralize the free alkali, phenolphthalein being used as indicator. According to this standard, which appears to be a fair one, three out of the seven samples reported could be considered satisfactory, while the four remaining samples exceed this limit from two to twelve times. The presence of sodium and mechanical impurities is due to excessive economy and carelessness. Potassium iodid is prone to decompose when not protected from atmospheric influences, and care should therefore be exercised in keeping it.

Sodium Hydroxid, by Alcohol.

This chemical, like potassium hydroxid of the same grade, should be carefully tested before using it for careful analytical work. Nothing more of particular interest is brought out by the results obtained.

Sodium Hydroxid, Pure.

The results reported support the belief that this quality of chemical is somewhat inferior to that made by the use of alcohol. Its impurities are more numerous and present in greater quantities.

Sulphuric Acid.

The first two samples are of good quality, but the last sample is contaminated with a lead compound, which indicates either that the acid has not been properly prepared or that the ordinary high-grade commercial article has been supplied.

L. F. Kebler,
A. L. Winton,
B. W. Kilgore,
Committee on the Testing of Chemical Reagents.

Mr. Davidson. I do not think the question of collaboration can be brought too often before the association. It should be considered the duty of every experiment station in the United States to take part at least in the work of some one referee. I heartily agree with what has been said in regard to the necessity for support in these investigations by the members.

Mr. Wiley. The matter of the purity of reagents has been brought home to this association by this report in a more pointed way than ever before. How many of our chemists test the purity of their reagents, and how many rely upon the manufacturer as to the character of the materials employed? I think the criticism to which in some cases our work has been subjected in foreign countries has been largely due to this one cause, namely, the failure to test the reagents employed, which of course affects the analytical results. Every chemist should resolve before leaving this meeting that he will not make another analysis for any work which is to be reported and published without assuring himself that his utensils are properly calibrated and that his chemicals are sufficiently pure. We must put aside the idea that an absolutely pure article can be obtained, but strive for a chemical containing only such a degree and kind of impurity as will not interfere with the results for which we are working.

At the close of this discussion a report on soils was presented by the referee.

REPORT ON SOILS.

By Cyril G. Hopkins, *Referee.*

At the last annual meeting of this association it was specifically recommended: "That the referee on soils be requested to make a thorough examination of the methods described in Bulletin 22 of the Bureau of Soils for the determination of available plant food."

It was understood, of course, that this examination was expected to deal primarily with the methods proposed and used by the Bureau of Soils for the determination of water-soluble plant food; but, in order that this investigation should be of the greatest value, it seemed advisable to the referee to include, for comparison, the determination of water-soluble plant food by the official methods, as well as by the methods used by the Bureau of Soils. For further comparison it seemed wise to make some determinations of available plant food by the two-hundredth normal hydrochloric-acid method, and also to ascertain the plant food soluble in strong hydrochloric acid, as determined by the regular official methods. It was hoped that the data thus obtained might furnish some information not only as to the accuracy of the different methods for the determination of the plant-food elements dissolved by the different solvents, but also help to ascertain whether any of the methods will give any indication of the comparative fertility of different soils.

During the consideration of the following report it is well to bear in mind the following direct quotations from Bulletin 22:

(1) Four constituents, calcium, potassium, phosphoric acid, and nitric acid, have generally been held to be the ones having the greatest practical significance for plant nutrition, and they are the ones which the demands of agriculture have brought into economic significance. It is therefore a cause of great satisfaction that, of the methods described above, those devised for these particular constituents are especially satisfactory. (2) That a chemical analysis of a soil, even by these extremely delicate and sensitive methods, will in itself give no indication of the fertility of this soil or of the probable yield of a crop, and it seems probable that this can only be determined, if at all, by physical methods, as it lies in the domain of soil physics.

There seemed little reason for investigating the methods for determining nitrogen or calcium, considering that soluble nitrogen in soils has long been determined by standard methods, that calcium as an element of plant food is no more significant than several other minor elements, and that it is not liable to be deficient in the soil. The work arranged for by the referee has, therefore, been confined mainly to the elements phosphorus and potassium. The investigations were divided into preliminary work and general work.

The referee begs to insert a word of explanation regarding the method of reporting results. While most stations report nitrogen on the basis of the element, some still report it as ammonia, while the Bureau of Soils of the United States Department of Agriculture reports it as the nitric acid radicle, NO_3. Most stations report potassium on the basis of potash, or K_2O, but all reports from the Bureau of Soils furnished to the referee have given the element as potassium, or K. (The fertilizer law of Illinois requires the element potassium to be reported in official analyses.) Most stations also report phosphorus as phosphoric oxid, P_2O_5, or phosphoric acid, falsely so called, but the results reported to the referee by the Bureau of Soils have given phosphorus on the basis of the phosphoric acid radicle, PO_4, while in Illinois the legal requirements compel us to report the element phosphorus, or P, in official analyses. For the sake of simplicity, all results given in the following report are reduced to the uniform basis of elements.

It seemed to the referee that it would be of very great value to the association in this investigation of methods if a more complete examination could be made of

the Rothamsted soil samples. These samples were originally secured from the Rothamsted experiment station by the Bureau of Chemistry, the Bureau of Soils having obtained samples from the Bureau of Chemistry. The quantity of soil remaining in these samples was too small to admit of its general use for distribution by the referee for the association work, but the Bureau of Chemistry was induced to furnish samples of three of the soils to the referee to be examined in the Illinois experiment station laboratory. These three samples are B 1 A, B 3 A, and W 10 A. The Rothamsted soil plat B 3 A has been fertilized with potassium salt annually for fifty years, but no phosphorus has been applied to it, and neither phosphorus nor potassium has been applied to B 1 A or W 10 A. Nitrogen fertilizers had been applied to all three of these plats.

The phosphorus and potassium determined in these three soil samples by Mr. W. F. Pate, of the Illinois station, using the regular official method with strong hydrochloric acid, gave the results shown in Table I.

TABLE I.—*Phosphorus and potassium in Rothamsted soils (official method with hydrochloric acid of 1.115 sp. gr.). Parts per million.*

Station.	Analyst.	Soil.	Fertilizer used.	Phosphorus.	Potassium.
Illinois	W. F. Pate	B 1 A		0.460	3,970
Do	do	B 3 A	Potassium	.490	4,370
Do	do	W 10 A		.490	3,930

The only point of special interest in this table is that the soil from plat B 3 A, which has been treated with potassium, contains 400 parts per million more of that element than the soil from plat B 1 A, which has grown the same crop (barley) and produced nearly the same yields during the past 50 years. This difference would amount to 1,080 pounds of potassium per acre, assuming that the soil sample was taken to a depth of 9 inches, which is the depth to which surface samples of Rothamsted soil have commonly been taken. This difference of 1,080 pounds of potassium is equivalent to an annual application of 200 pounds of potassium sulphate for 27 years. It would be of interest to know whether the composition of the subsurface soils and subsoils from these same plats would also show a difference in potassium content, which seems altogether probable, considering the degree of solubility of potassium compounds in soil water.

Table II shows the phosphorus and potassium dissolved in two-hundredth normal hydrochloric acid from these three Rothamsted soils, as determined by Mr. Pate, of the Illinois station.

TABLE II.—*Phosphorus and potassium in Rothamsted soils (official method with N/200 hydrochloric acid). Parts per million.*

Station.	Analyst.	Soil.	Fertilizer used.	Phosphorus.	Potassium.
Illinois	W. F. Pate	B 1 A		1.3	Lost.
Do	do	B 3 A	Potassium	1.4	144.1
Do	do	W 10 A		1.5	31.5

It will be observed that between 1 and 2 parts of phosphorus per million of soil are dissolved in the dilute acid; also that 144.1 parts of potassium were obtained from soil B 3 A, to which potassium fertilizer has been applied, while only 31.5 parts of potassium were dissolved from soil not so fertilized, thus showing that this method of analysis furnishes some information regarding the fertility of the soil.

Determinations of water-soluble plant food by official methods were made by Mr. I. O. Schaub, of the Illinois station, upon these three samples of Rothamsted soils, using the method proposed by the Bureau of Soils for making the solution. Table III gives the results obtained.

TABLE III.—*Phosphorus and potassium in Rothamsted soils (official method with water solution). Parts per million.*

Station.	Analyst.	Soil.	Fertilizer used.	Phosphorus.	Potassium.
Illinois	I. O. Schaub	B 1 A		1.2	28.3
Do	do	B 3 A	Potassium	1.9	68.4
Do	do	W 10 A		1.8	23.7

From 1 to 2 parts of phosphorus are obtained, and we observe that from two to three times as much potassium is dissolved from soil B 3 A as from the soils which have not received potassium fertilizer.

The results reported in Table IV, obtained by Mr. Schaub, of the Illinois station, show the phosphorus and potassium from these Rothamsted soils as determined by the colorimetric methods proposed by the Bureau of Soils, as subsequently modified by Schreiner.[a]

TABLE IV.—*Phosphorus and potassium in Rothamsted soils (colorimetric method with water solution). Parts per million.*

Station.	Analyst.	Soil.	Fertilizer used.	Phosphorus.	Potassium.
Illinois	I. O. Schaub	B 1 A		19.7	15.4
Do	do	do			8.2
Do	do	do			9.2
Do	do	B 3 A	Potassium	15.2	35.8
Do	do	do	do		30.7
Do	do	do	do		37.8
Do	do	W 10 A		16.1	6.1
Do	do	do			8.2
Do	do	do			9.2

It will be observed that the results obtained on phosphorus are about ten times as high by the colorimetric as by the official method; also that the potassium in sample B 3 A is very much higher than in the soils not fertilized with potassium, as has been shown by every method of analysis, including the colorimetric method in the hands of the Bureau of Soils.

For the general work the referee selected two soils.

Soil No. 1.—The soil which is marked No. 1, in the following report, is one of the soils used last year by Mr. C. B. Williams, the associate referee on phosphoric acid. It is correctly described by him as follows:[b]

This is a dark soil, containing considerable humus to the depth of 7 inches, taken from the terrace or second bottom land along the Dupage River, in Dupage County, Ill. It lies from 20 to 30 feet above high-water mark, and probably has not been overflowed for centuries, although it may have at one time been bottom land of the Dupage River. It is made up of glacial drift, somewhat modified by the underlying limestone deposits. It belongs to one of the richest classes of agricultural soils of the State of Illinois. The land has been in alfalfa for three years and has produced as high as 10.5 tons of alfalfa hay per acre in a single season. Under favorable seasonal conditions, says Mr. Cyril G. Hopkins, who furnished the soil, it will undoubtedly produce from 90 to 100 bushels of corn per acre.

[a] J. Am. Chem. Soc. 25: 1056.

[b] Bulletin No. 81, Bureau of Chemistry, being the proceedings of this association for 1903, page 166.

Soil No. 2.—This soil is a gray silt loam representing large areas of cultivated land in southern Illinois. The sample collected represents the better phase of the extensive type to which it belongs. It is made up of loessial material overlying, and perhaps somewhat modified by, glacial drift. The sample used for these investigations was collected from the level prairie land in Perry County, Ill., although the same type of soil occupies extensive areas in more than 20 other counties in southern Illinois. Under favorable seasonal conditions this soil is capable of producing from 25 to 40 bushels of corn peracre and corresponding yields of other crops.

Neither of the samples used for the association work had been analyzed previous to the distribution to the several analysts, aside from the phosphorus determinations on No. 1 reported to the association last year, but of course the general productive capacity and the average composition of each type were well known to the referee.

The cooperating analysts were requested to analyze the two soils, especially for phosphorus and potassium, by each of the four methods mentioned in the beginning of this report, namely:

(1) By the regular official methods, using hydrochloric acid of 1.115 specific gravity as the solvent.

(2) For available plant food, using two-hundredth normal hydrochloric acid for the solvent and completing the determinations by the official methods.

(3) For water-soluble plant food, making the solution as proposed by the Bureau of Soils in Bulletin 22, but completing the determinations by the official standard methods of this association.

(4) For water-soluble plant food, making the solution as in No. 3 and completing the determination by the colorimetric methods advocated by the Bureau of Soils.

At the time the soil samples were sent out it was assumed that the annual meeting would not be held before October or November, but it was suggested by the referee that if possible the results should be reported by September 15, or at latest by October 1. After the date for this meeting had been fixed, a subsequent letter was sent to the cooperating analysts urging that the results be transmitted in time for this report.

It is regretted that many analysts who expected to participate in this investigation have been unable to do so owing to various obstacles, usually beyond the control of the analyst himself. The following laboratories have furnished some results in time for this report:

The Bureau of Soils, reported by F. K. Cameron.

The Virginia experiment station, reported by R. J. Davidson.

The Kentucky experiment station, reported by A. M. Peter.

The Minnesota experiment station, reported by Harry Snyder.

The Indiana experiment station, reported by W. J. Jones, jr.

The Illinois experiment station, reported by J. H. Pettit.

The following tables give the results received, arranged for comparison on the uniform basis of elements in parts per million of dry soil:

TABLE V.—*Plant food elements in soils. Parts per million.*

[Method: Official, using hydrochloric acid of 1.115 sp. gr. as solvent.]

Station.	Analyst.	Nitrogen.		Phosphorus.		Potassium.	
		Soil No. 1.	Soil No. 2.	Soil No. 1.	Soil No. 2.	Soil No. 1.	Soil No. 2.
Virginia	J. H. Gibboney	6,380	1,280	1,000	680	4,050	2,300
Kentucky	I. D. Averitt	7,760	1,340	1,190	400	4,570	2,320
Indiana	C. S. McGovney	7,210	1,220	1,130	550	4,230	1,940
Illinois	W. F. Pate	7,400	1,330	1,170	520	4,970	2,680
Average		7,190	1,290	1,120	540	4,450	2,310

From the data given in this table it will be seen that No. 1 contains five times as much nitrogen and twice as much phosphorus and potassium as No. 2. Both are normal cultivated soils, and the difference in chemical composition is in accord with the well-known difference in their productive capacity.

Table VI shows the amounts of phosphorus and potassium dissolved from these soils by two-hundredth normal hydrochloric acid, the determinations being made by the official methods.

TABLE VI.—*Available plant food in soils. Parts per million.*

[Method: Official, using N/200 hydrochloric acid as solvent.]

Station.	Analyst.	Phosphorus.		Potassium.	
		Soil No. 1.	Soil No. 2.	Soil No. 1.	Soil No. 2.
Virginia	J. H. Gibboney	2.3	1.4	34.0	29.1
Kentucky	I. D. Averitt	2.1	Trace.	38.3	29.4
Illinois	W. F. Pate	2.1	1.1	62.9	37.8
Do	do	2.2	1.0	60.7	37.1
Do	do	2.1	.9	.....	.....
Do	do	2.3	.....	.....	.....

There is a satisfactory agreement on the phosphorus determinations and on the results as a whole in showing larger quantities of available plant food in the better soil, but it will be noted that the Illinois station obtained much larger amounts of potassium than were obtained by the two other stations, which are in fairly close agreement.

Table VII shows the water-soluble phosphorus and potassium in these soils extracted by the method used by the Bureau of Soils and determined by the official methods of this association.

TABLE VII.—*Water-soluble plant food in soils. Parts per million.*

[Method: Official, using water as solvent.]

Station.	Analyst.	Phosphorus.		Potassium.	
		Soil No. 1.	Soil No. 2.	Soil No. 1.	Soil No. 2.
Virginia	J. H. Gibboney	1.1	0.7	20.4	13.9
Kentucky	I. D. Averitt	.9	Trace.	29.1	17.4
Bureau of Soils		.9	Trace.	16.1	8.4
Minnesota	J. A. Hummel	.....	.....	23.2	9.1
Indiana	C. S. McGovney	6.0	.6	.....	.....
Illinois	I. O. Schaub	3.4	.8	35.6	21.6
Do	do	3.5	.8	35.1	23.2
Do	do	3.7	.7	36.3	21.5

The results of all analysts agree that soil No. 1 furnishes the larger amounts of water-soluble plant food. There is a good agreement on phosphorus determinations, excepting the results from Indiana and Illinois on soil No. 1, which are much higher than those reported by Virginia, Kentucky, or the Bureau of Soils. There are marked variations among the results on potassium, but the fact that duplicate and triplicate determinations by the same station agree well, and the further fact that there is a general agreement as to the relative amounts of potassium dissolved from one soil as compared with the other, indicate that these differences are due to the lengths of time required in filtration during which the soil remains in contact with the solvent, or to other similar causes.

Table VIII gives the water-soluble phosphorus and potassium extracted as in Table VII, but determined in the water extract by the colorimetric methods of the Bureau of Soils.

TABLE VIII.—*Water-soluble plant food in soils. Parts per million.*

[Method: Colorimetric, using water as solvent.]

Station.	Analyst.	Phosphorus.		Potassium.	
		Soil No. 1.	Soil No. 2.	Soil No. 1.	Soil No. 2.
Bureau of Soils		0.7	0.1	16.3	8.0
Do				15.0	7.9
Do				16.2	
Minnesota	J. A. Hummel			33.2	20.8
Illinois	I. O. Schaub	[a]18.8	[a]8.9	13.9	10.2
Do	do	[a]20.6	[a]8.9	18.2	5.1
Do	do	[b]15.0	[b]9.8	19.3	6.1
Do	do	[b]20.6	[b]15.1	22.6	6.1

[a] Silica previously removed. [b] Silica not removed.

Even by this method we find a relative agreement in the determinations as between the two soils, but wide differences on each soil not only between analysts, but, in the case of the Illinois station, between different determinations by the same analyst.

It is to be regretted that so few analysts were able to make the determinations by the colorimetric methods. In the phosphorus work results were reported only by the Bureau of Soils and the Illinois station. It will be noted that the Bureau of Soils obtained 0.7 part of phosphorus per million of soil from soil No. 1 and 0.1 part from soil No. 2, while the Illinois station obtained from 15.0 parts to 20.6 parts from soil No. 1 and from 8.9 parts to 15.1 parts from soil No. 2. Mr. Schaub, of the Illinois station, reports that by simply reducing the standard of comparison to one-half strength he obtained a reading as low as 6.6 parts of phosphorus on soil No. 1 and 6.2 parts on soil No. 2, the silica not being removed; and a reading of 2.8 parts of phosphorus instead of 18 to 20 parts on soil No. 1, and a reading of 1.8 parts instead of 8.9 parts on soil No. 2, when the determinations were made after the removal of silica, a standard of one-half strength being used.

It seems appropriate to call attention to the fact that the colorimetric method usually gives much higher results than were obtained by the Bureau of Soils in this investigation, as is evidenced by the fact that among all the results reported in Bulletin 22 on the Rothamsted soils and on more than fifty different type soils, collected from many different parts of the United States, there is no record of a phosphorus determination so low as that reported by the Bureau of Soils on our soil No. 1, and this is seven times the amount reported on soil No. 2.

COMMENTS REPORTED TO THE REFEREE.

F. K. Cameron.—In Bulletin No. 22, Bureau of Soils, U. S. Department of Agriculture, is described an attempt to follow the changes which take place in the soluble mineral content of the soil at any given spot from time to time throughout the growing season and to correlate the results with the development of the crop. A single examination of a soil can not be expected to have any particular bearing on the problem. The work on the samples submitted by the referee, Mr. Hopkins, was therefore confined to analyses of the aqueous extracts of the soils by gravimetric methods and by colorimetric methods described in Bulletin 22. The gravimetric procedures were those prescribed by the Association of Official Agricultural Chemists.

All gravimetric determinations were made by one asssistant, the colorimetric determinations of phosphates were made by a second assistant, and the colorimetric

determinations of potassium by a third, in a manner similar to that employed in the verification of the phosphate method.[a] No one of the analysts knew the results of the others until all the results had been handed in. For the gravimetric determinations 1,500 cc portions of the solutions were used; for the colorimetric determinations 25 or 50 cc portions were used. The solutions were made by treating the soil with distilled water in the proportion of 1 part of soil to 5 parts of water, by weight, filtering through a Pasteur-Chamberland filter. The aqueous extract from sample No. 1 was quite highly colored, and sample No. 2 was slightly colored. The extract of sample No. 1 when treated a second time with carbon black yielded a clear and perfectly colorless solution, an essential condition before developing the test color. With both extracts the amount of phosphates was so small that possibly the modification of the method recently used with success by Lincoln and Barker at the University of Illinois[b] might have proved advantageous. In view of the color of the solutions the procedure described at the Providence meeting of the American Chemical Society[c] could undoubtedly have been used to advantage, thus avoiding the labor of decolorizing.

Harry Snyder.—Comparisons were made of the official and the colorimetric methods for the determination of potash. The solutions were prepared as recommended by

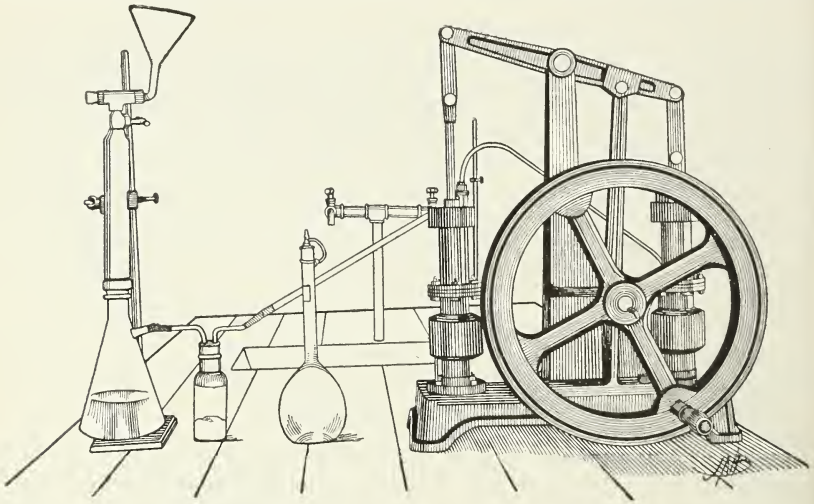

FIG. 2.—Apparatus used in soil analysis by Harry Snyder, Minnesota station.

the referee. The soil solution, however, was passed through a Pasteur-Chamberland filter in addition to the usual filtration. The filter was connected with a large Erlenmeyer filtration flask, which in turn was connected with a vacuum pump as shown in the illustration. By this means 800 cc of the clear filtrate was obtained in 30 to 40 minutes.

In the gravimetric method all of the separations were made as prescribed by this association. The final product, however, was weighed as platinum collected on platinum electrodes by the well-known methods of electrolysis instead of being weighed as potassium platinic chlorid.

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[a] The Determination of Phosphates in Aqueous Extracts of Soils and Plants; Oswald Schreiner, J. Am. Chem. Soc., 1904, *26:* 808.

[b] Determination of Phosphates in Natural Waters; J. Am. Chem. Soc., 1904, *26:* 975.

[c] The Colorimetric Estimation of Phosphates, Second Method; Oswald Schreiner and B. E. Brown, Science, 1904, *20:* 44.

Tests were made to determine the influence of the presence of calcium and magnesium salts, inasmuch as the colorimetric method fails to make adequate provision for their complete removal. About 100 milligrams each of calcium and magnesium sulphate were added to distilled water and the potash was determined by the colorimetric process; a decided color was obtained, equal in intensity to 5 parts per million of potash (K_2O). The salt used when tested by the official method failed to give any reaction for potash. Both calcium and magnesium form well-known salts with platinum.

The results obtained by the colorimetric method for the determination of potash appear to be relative rather than absolute. Larger quantities of soil solution should be used and provision should be made for the complete removal of lime and magnesium salts so as to secure greater accuracy for the colorimetric method.

C. S. McGorney.—The nitrogen, phosphoric acid, and potash were obtained by a strict adherence to the official methods given in Bulletin 46, save that in the potash determination the last traces of barium and lime were removed with ammonium sulphate and ammonium oxalate, respectively, with intervening filtration. On the water-soluble phosphoric acid the preliminary filtration of the soil solution required 1 hour in the case of No. 1 and 2 hours in the case of No. 2, obtaining 750 cc in each case. No. 1 filtered clear, while No. 2 was not entirely clear after repeated filtrations.

Only single precipitations with molybdate and magnesia mixtures were made for the water soluble phosphates nor were the ignited residues examined for purity.

J. H. Pettit.—All water soluble solutions were obtained by means of the Pasteur-Chamberland filter and the solutions for colorimetric phosphorus were decolorized by shaking with lampblack; in the case of soil No. 1, three and four treatments were necessary to give a colorless solution. All gravimetric and volumetric results which seemed at all unusual from comparison with other work have been repeated, in all cases giving good agreement with the first results.

Colorimetric results on phosphorus are reported both by the method of Bulletin 22, Bureau of Soils, and by the method suggested by Oswald Schreiner.[a]

Neither Mr. Schaub nor myself has any confidence in any of the colorimetric results reported. After working with the methods five weeks and looking up the available literature we are not able to get concordant results twice in succession on the same solution, though sometimes duplicates will agree fairly well.

In the potassium method, under some conditions which we have not discovered, we get with the same solution a greater development of color than under others. A blank run on distilled water gives a readable color and one run with sulphuric acid, as in the regular method, gives considerable color. It seems to be impracticable to wash on a filter a precipitate which can scarcely be seen without danger of loss by solubility in the wash water or by passing through the pores of the filter. The washing of the minute potassium platinic chlorid precipitate is evidently one of the weak points of the method.

In the colorimetric method for phosphorus we find, as was early pointed out by Veitch,[b] that the reagents nitric acid and ammonium molybdate alone give a yellow color, and hence it is necessary to have approximately the same amounts of these reagents in both the solution being read and in that part of the standard which is used in the reading. This necessitates a preliminary determination to calculate the amounts of reagents to be used in the final determination.

The two methods used give comparable results, but when the strength of the standard is varied, the results are not at all comparable.

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[a] J. Amer. Chem. Soc., *25:* 1056.

[b] Ibid., 169.

A. N. Peter.—In the determinations made on the solution in two-hundredth normal hydrochloric acid, we did not follow exactly the method of determining the potash and phosphoric acid described in paragraph 5 of your letter, because I suppose that was intended more especially for the colorimetric determination of phosphoric acid. We evaporated only once to dryness for the separation of silica and then determined the phosphoric acid volumetrically in an aliquot of the solution and determined the potash in another aliquot by the gravimetric method with platinum chlorid as usually done in this laboratory. We have made for comparison a determination of the phosphoric acid and potash dissolved by digestion in fifth normal nitric acid for 5 hours at the room temperature, shaking every half hour. This is the method we have been following here and it seems to give results that are in fair agreement with the agricultural capabilities of the soil.

Method used in the Kentucky laboratory.

Determinations and method.	Sample No. 1.	Sample No. 2.
Phosphorus by digestion in fifth normal nitric acid 5 hours at room temperature...	67	11
Potassium, same	235	91

(I) Water-soluble phosphorus and potassium by method of the referee (official). In these determinations the turbid filtrate from the soil was cleared by adding a few drops of nitric acid and filtering again. Aliquots corresponding to 75 grams of soil were taken. The phosphorus was determined by the volumetric method, though the quantity present was too small for a satisfactory determination.

(II) An experiment was made by digesting 140 grams of soil (calculated on water-free basis) with 7 liters of two-hundredth normal hydrochloric acid and an extra amount of hydrochloric acid equivalent to the alkalinity of the soil as shown by a preliminary digestion having been added. The room temperature was used, about 25° C, and the bottles were shaken about every half hour for 5 hours. Aliquots corresponding to 60 and 55 grams were taken for phosphorus and potassium, respectively, and gave the following:

Experiment with increased volume of hydrochloric acid.

Determinations and method.	Sample 1.	Sample 2.
Phosphorus dissolved, N/200 HCl	4.7	0.4
Potassium dissolved, N/200 HCl	224	116

The extra acid added to correct the alkalinity of the soils was 72.8 cc normal hydrochloric acid in No. 1 and 8.4 cc in No. 2. This was mixed with the 7 liters before making up the volume, so it was counted as so much water, i. e., there was to be 7 liters of acid, which would be two-hundredth normal, after the calcium carbonate, etc., of the soil had been acted upon. It is to be noted that a similar procedure was followed in the experiments with fifth normal nitric acid already reported, but not in the case of the experiments with two-hundredth normal hydrochloric acid according to the referee's directions as already reported. (See Table VI.)

My reason for trying the larger volume of two-hundredth normal hydrochloric acid is that I do not think the action of 1 liter of two-hundredth normal acid on 200 grams of soil could be effective enough to show up properly the capabilities of a very rich soil. It approached too closely to the action of water, which has to be long continued and used in large quantity to bring out these differences.

Recommendations.

It is recommended—

(1) That the investigation of methods for the determination of water-soluble plant food be continued.

(2) That methods be investigated for the determination of the readily soluble plant food in soils, using acid of greater strength than two-hundredth normal, as recommended by the referee for last year and briefly reported upon by Professor Peter in the preceding pages.

(3) That this association encourage the reporting of soil analyses, so far as practical, upon the uniform basis of chemical elements.

At the conclusion of the report on soils, further papers on the subject and discussion were in order. Messrs. Fraps and Veitch presented the following papers and there was a discussion on the liming of soils which is given in part, Messrs. Wheeler, Veitch, Hopkins, and Wiley being the participants.

NITRIFICATION AND SOIL DEFICIENCIES.

By G. S. Fraps.

It is well known that nitrification in a given soil depends to a large extent upon physical properties—moisture, temperature, looseness of the soil, etc. That different soils vary in their capacity for converting nitrogenous bodies into nitrates under similar physical conditions has also been established,[a] and a method has been proposed for comparing soils in this respect. Withers and Fraps[b] applied this method to North Carolina soils and found a variation from 11 to 106 in relative nitrifying power. The author has recently devoted some time to a study of the cause of this variation. An attempt will be made to present briefly some of the more important results of this work, reserving details for subsequent publication.

Effect of Water.

The effect of varying amounts of water was determined on two soils. The maximum effect was with 3/9 of the water capacity of a clayey soil, and with 5/9 of the capacity of a sandy soil. With 7/9 and 9/9 denitrification occurred in the first instance and only a very small amount in the second.

Effect of Calcium Carbonate.

The effect of calcium carbonate was studied in thirteen soils. No increased production of nitrates occurred in two soils; in the others, placing the amount of nitrates formed in the soil without calcium carbonate at 100, with calcium carbonate the nitrates were graded from 125 to 340. These soils must be considered as deficient in calcium carbonate as far as nitrification under the conditions of the experiment is concerned. No relation could be traced between the acidity of the soil according to the Hopkins method and the effect of calcium carbonate on nitrification (see Table I). The soil with the greatest acidity indeed responded most of all to the calcium carbonate, but soils of low acidity were also decidedly affected by the same substance. While, therefore, it is probable that nitrification is always increased by calcium carbonate in acid soils, soils which are not acid may also exhibit a decided increase in the same way.

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[a] Fraps, Am. Chem. J., *29:* 233.

[b] Rep. North Carolina Agr. Exper. Stat., 1902–3.

TABLE I.—*Effect of calcium carbonate on nitrification and acidity of soil.*

Soil No.	Nitrification.		Acidity.
	Without calcium carbonate.	With calcium carbonate.	
			Parts per million.
76	100	92	40
132	100	100	14
112	100	125	00
159	100	130	.....
128	100	150	18
129	100	150	50
137	100	167	113
131	100	200	9
135	100	200	14
102	100	208	5
97	100	300	45
141	100	340	342

Since one function, at least, of the calcium carbonate is to neutralize the acid produced by nitrification, an attempt was made to trace some relation between the basicity of the soil and the effect of calcium carbonate. Basicity was determined by three methods:

(1) Ten grams of soil were treated with 100 cc of fifth normal nitric acid 12 hours, and 10 cc of the filtrate titrated with caustic soda and phenolphthalein. Basicity due to salts of iron and aluminum are not included, as they are precipitated during the titration. The basicity so measured is due to carbonates and easily decomposed silicates.

(2) Fifty grams of soil were treated with 100 cc of tenth normal nitric acid half an hour, and 20 cc of the filtrate titrated with caustic soda and methyl orange.

(3) After titrating as in (2), phenolphthalein was added, and the titration continued until the solution became pink.

No relation could be traced between basicity measured as described, and the effect of calcium carbonate upon nitrification. Other factors besides basicity may enter into the action of this substance.

TABLE II.—*Basicity of soils and effect of calcium carbonate on nitrification.*

Soil No.	Nitrification.		Basicity as calcium carbonate.		
	Without calcium carbonate.	With calcium carbonate.	Method 1.	Method 2.	Method 3.
			Per cent.	*Per cent.*	*Per cent.*
76	100	92	0.10	0.11	0.06
132	100	100	4.64	1.10	1.05
112	100	125	.72	.60	.55
159	100	130	3.94	1.10	1.05
128	100	150	.77	.50	.40
129	100	150	.35	.47	.18
137	100	167	1.05	.61	.50
131	100	200	.29	18	.07
135	100	200	.24	.18	.10
102	100	209	.20	.23	.14
97	100	300	1.14	.73	.59
141	100	340	.25	.30	.22

If the entire amount of nitrogen added to the soil were oxidized, 0.21 per cent of calcium carbonate would have been required to neutralize the acid so formed.

Effect of Phosphoric Acid.

The effect of phosphoric acid in the form of acid phosphate and of potash as potassium sulphate were tested upon fifteen soils. Acid phosphate, alone or with calcium carbonate, produced an increase of nitrification in thirteen of the fifteen soils; in two soils there was a decrease. In four of the twelve soils acid phosphate alone decreased nitrification, but increased it in the presence of calcium carbonate. We would judge from the results that, as far as nitrification under the conditions of the experiment is concerned, phosphoric acid is deficient in thirteen of the fifteen soils.

Table III.—*Effect of phosphoric acid on percentage of added nitrogen converted into nitrates.*

Soil No.	Without calcium carbonate.			With calcium carbonate.		
	Without acid phosphate.	With acid phosphate.	Increase.	Without acid phosphate.	With acid phosphate.	Increase.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
76	2.6	10.9	8.3	2.4	11.5	9.1
131	14.1	21.0	6.9	29.6	34.6	5.0
132	38.6	42.3	3.7	38.3	.....	.....
135	5.8	8.3	2.5	12.2	22.8	10.6
112	14.7	28.6	13.9	17.7	29.0	15.1
102	7.9	9.7	1.8	16.5	.....	.....
129	23.7	19.9	− 3.8	36.9	46.5	9.6
141	10.2	8.1	− 2.1	34.5	42.6	8.1
128	40.7	27.4	−13.3	60.4	56.4	−4.0
97	11.5	8.6	− 2.9	31.9	36.6	4.7
108	14.3	36.7	22.4	.....	.....	.....
110	50.5	53.7	3.7	.....	.....	.....
137	16.1	12.0	− 3.9	26.9	25.4	−1.5
159	8.1	24.8	16.7	10.5	.....	.....
165	8.6	.....	.....	18.9	19.9	1.0

Effect of Potash.

In nine of the fifteen soils potash produced an increase in nitrification, though the increase was not large in two cases. We would judge from these experiments that, as far as nitrification under the conditions is concerned, these nine soils are deficient in potash.

TABLE IV.—*Effect of potash on percentage of added nitrogen converted into nitrates.*

Soil No.	Without potash.	With potash.	Increase or decrease.
	Per cent.	*Per cent.*	*Per cent.*
76	2.6	9.0	6.4
131	14.1	20.1	6.0
132	38.3	39.8	1.2
135	5.8	15.7	9.9
112	14.7	29.8	15.1
102	7.9	9.7	1.8
129	23.7	21.9	−1.8
141	10.3	9.3	−1.0
128	40.7	39.9	−0.8
97	11.5	8.3	−3.2
108	14.3	14.7	0.4
110	50.5	54.6	4.1
137	16.1	17.7	1.6
159	8.1	5.6	−2.5
165	[a] 18.9	[a] 10.0	−8.9

[a] With calcium carbonate.

EFFECT OF PHOSPHORIC ACID AND POTASH.

In the few cases in which phosphoric acid and potash were added together to the soil, decreased nitrification over one or the other alone resulted. This was perhaps due to the excess of soluble salts so added retarding activity of nitrification.

NITRIFICATION AND POT EXPERIMENTS.

It was considered possible that soils which were deficient in phosphoric acid or potash for nitrification would also be deficient in these elements for some of the higher plants. Pot experiments on corn and cotton were accordingly made to test this point. Unfortunately the amount of each sample of soil available was not sufficient to allow the use of duplicate pots. According to Vanderyst[a] the results of the physiological analysis of a soil made in this way vary with the species, variety, and sometimes the individuality of the plant, the quality of the seed, the physical conditions of the soil and air, and the form in which the fertilizers are applied. Only with due caution, therefore, can this be used as a test for any method.

As far as potash is concerned, the pot experiments brought out no relation between the effect of potash on nitrification and on cotton. The pot experiments seemed to show that the soils did not need this element for cotton. Plants differ in their power to get food from the soil, however, and it is possible that with plants of weaker assimilative capacity for potash some relation could be traced between the effect of potash upon nitrification and the requirements of this plant for potash.

In the case of phosphoric acid, ten of the twelve soils which needed phosphoric acid for nitrification also showed the need of phosphoric acid by pot tests. In one of these the gain of dry matter produced by the phosphoric acid was not in satisfactory relation to the gain of nitrification and it will be excluded. Two of the twelve soils showed a gain of dry matter produced by phosphoric acid but not a gain of nitrification.

[a] Exper. Stat. Rec., *15*: 759.

TABLE V.—*Effect of phosphoric acid on nitrification and on cotton.*

Soil No.	Added nitrogen converted to nitrates (with calcium carbonate).			Weight of crop (water-free).		
	Without acid phosphate.	With acid phosphate.	Increase.	Potash and nitrogen.	Potash, phosphoric acid, and nitrogen.	Increase.
	Per cent.	*Per cent.*	*Per cent.*	*Grams.*	*Grams.*	*Grams.*
76	2.4	11.5	9.1	[b]4.7	[b]9.2	[b]4.5
131	29.6	34.6	5.0	[b]3.1	[b]14.1	[b]11.0
135	12.2	22.8	10.6	15.3	18.2	2.9
129	36.9	46.5	9.6	.9	3.3	2.4
141	34.5	42.6	8.1	2.4	3.6	1.2
97	31.9	36.6	4.7	3.1	6.9	3.8
[a]108	14.3	36.7	22.4	2.9	6.1	3.2
[a]110	50.5	53.7	3.2	4.2	5.3	1.1
[a]159	8.1	24.8	16.6	4.0	4.4	.4
128	60.4	56.4	− 4.0	3.1	4.9	1.8
137	26.9	25.4	− 1.5	2.5	4.9	2.4

[a] Without calcium carbonate. [b] Corn.

From these results we feel justified in saying that the soil deficiency in phosphoric acid as revealed by nitrification tests, under the conditions of these experiments, is at least an indication that the soil needs phosphoric acid for some of the higher plants. It must be remembered that plants vary in power of assimilating phosphoric acid from the soil and that the results of a pot test with fertilizers vary with the kind of plant and other conditions. We do not wish to propose nitrification tests as a method for determining soil deficiencies; a large amount of further investigation must be made before such a statement can be definitely made. The nitrification test appears to be a valuable indication, however.

CONCLUSION.

In this paper it has been shown that the varying power of soils to transform organic matter into nitrates under comparable physical conditions is due, in part, to deficiency in available calcium carbonate, potash, or phosphoric acid. Other causes, as yet undetermined, are of influence, probably, since we have not yet been able to raise the soils of lowest nitrifying power to the rank of the highest.

We have also shown that a deficiency in phosphoric acid for nitrification is, as a rule, accompanied in the cases under observation by a deficiency in phosphoric acid for corn and cotton.

Evidently investigation into the causes of the variation in nitrifying powers of soils, and the relation between soil deficiencies, as shown by nitrification and pot experiments, has a very important bearing upon the problems of soil chemistry and the maintenance of the fertility of the soil.

SUMMARY OF EXPERIMENTS ON THE RELATION OF SOIL ACIDITY TO FERTILITY.

By F. P. VEITCH.

During the past two years, by the instructions of the chief of the Bureau of Chemistry, I have continued the investigation of the relation of the acidity of the soil to fertility, and have endeavored to devise methods for the detection and estimation of this condition. This work has been done partly with the soils upon which the Bureau of Chemistry has been conducting its vegetation experiments for the past eight years, partly in cooperation with the Maryland station, partly by independent field experi-

ments, and partly by pot experiments conducted for this specific purpose. By thus using several independent experiments and lines of work it has been possible to develop the methods in a much shorter time than would otherwise have been necessary and to connect the work directly with practical farm experience. I desire to give the association a summary of our results and of the more important conclusions to which they point and it is hoped to present these later in greater detail.

The results of our investigation of methods for determining acidity have already been published, [a] and while the method proposed lacks the delicacy and the speed which are so attractive to chemists, by it we can determine the total apparent acidity of soils, and the results thus obtained seem to have a practical significance.

The results of the work may be thus summarized:

In box experiments all of the more common field and garden crops have given larger and more healthy plants on alkaline sandy soil than on the same sand somewhat acid from sulphuric acid or acid sulphate.

In pot experiments red clover and cowpeas have given larger crops on a soil acid from insoluble organic matter only, when such acidity is completely neutralized than when partially neutralized. Red clover has given the largest yields on all kinds of soils tried when the acidity was completely neutralized.

Observations made on the plots partially and completely neutralized at the Maryland experiment station have generally shown higher yields on the completely neutralized plots. This is particularly true of red clover, where this year from equal areas on the several plots the following dry weights were obtained:

TABLE I.—*Crops of red clover grown on acid and alkaline soils.*

Number of plots.	Amount of calcium oxid applied.	Reaction.	Weight of crop (dry material).
	Bushels.		*Grams.*
1	10	Acid	7
2	20	do	7
3	0	do	4
4	30	do	27
5	40	Alkaline	28
7	50	do	69
8	60	do	72

The increased yield of some of the crops has not been economically obtained, though the average increase has been.

A careful examination of the soils and tabulations of Mr. Moore's analytical data obtained in the vegetation experiments, which have been conducted under the direction of the chief of the Bureau since 1895 on soils and subsoils from many parts of the country, brings out the following facts:

TABLE II.—*Increase of average crops grown on alkaline soils and subsoils over those grown on acid soils and subsoils.*

Crop.	Increase on alkaline over acid—	
	Soil.	Subsoil.
	Per cent.	*Per cent.*
Oat	33	77
Buckwheat	21	18
Bean	41	38

[a] J. Am. Chem. Soc., *26*: 627.

The average amount of nitrogen removed by these crops has been from 17 to 70 per cent greater on alkaline soils.

The percentage of nitrogen in the crops has been from 0.01 to 0.43 per cent less on alkaline soils.

The amount of potash removed has been from 12 to 99 per cent greater on alkaline soils.

The percentage of potash in the crops has been from 0.04 to 0.72 per cent greater on alkaline soil in the oat crop and in the buckwheat crop following it, and from 0.02 to 0.37 per cent less in the bean crop and the buckwheat following it.

The average amount of phosphoric acid removed has been from 40 to 356 per cent greater on alkaline soils.

The percentage of phosphoric acid in the crops has been from 0.02 to 0.3 per cent greater on alkaline soils.

In other words, alkaline soils have given the largest crops, have yielded more plant food, a given amount of which has been used more economically, except in the case of phosphoric acid, and have produced more crops than have acid soils.

TABLE III.—*Average amounts of phosphoric acid and potash removed from alkaline and acid soils by different crops.*

Crop.	Plant food removed by crop.	Amount of plant food removed from—	
		Alkaline soils.	Acid soils.
		Per cent.	*Per cent.*
Oats	Phosphoric acid	0.0011	0.0008
Buckwheat, following oats	do	.00079	.0006
Beans	do	.00096	.0006
Buckwheat, following beans	do	.0009	.0005
Oats	Potash	.0045	.0037
Buckwheat, following oats	do	.0029	.0027
Beans	do	.0031	.0025
Buckwheat, following beans	do	.0037	.0030

The average solubility of phosphoric acid in two-hundredth normal hydrochloric acid in alkaline soil was 0.0009 per cent; in acid soil, 0.0006 per cent. The average solubility of potash in two-hundredth normal hydrochloric acid in alkaline soil was 0.0091 per cent; in acid soil, 0.0074 per cent.

The amount of nitrogen removed from alkaline soil indicates a more rapid nitrification there than in acid soil, but the percentage composition of crops grown on acid soil indicates that lack of nitrification was not the controlling factor in the crop yield. More than sufficient nitrogen for the crop produced appeared to be at the command of the plants even on the most acid soil.

Different plants affect the reaction of the soil to different degrees. In six years oats followed by buckwheat had decreased the total apparent acidity of nearly all the soils, making some of them alkaline in reaction. On the other hand, beans followed by buckwheat in the same time increased the total apparent acidity of the soils, rendering some originally alkaline soils acid. Whether this different effect is due to the different amounts of residues left in the soils by different crops, to difference in amount of lime required by the crops, or to the activity of nitrogen fixing organism, we have not attempted to determine.

Fungus diseases which have more or less visibly affected the bean crop since the early years of the experiments were carefully looked for in 1899. No evidence of injury from this cause was found on the plants grown on alkaline soils, while fungus

(*Fusarium*) was found in the plants grown on every acid soil except two. The pots were in the same house, had been worked with the same tools, and no precaution had been taken to prevent infection.

In this connection we do not advance the argument that plants on alkaline soils will not suffer from fungus diseases, but it is believed that the dangers of serious infection and injury to crops are much less on such soils than on acid soils.

While these experiments, as well as those made by others, have shown that most of our common field and garden crops will not stand much free acid in the soil (in a sandy soil well supplied with available plant food and lime as sulphate all plants were killed in two months by acid equal to 500 parts of calcium oxid per million, and most were seriously affected by 250 parts), we can trace no close relation between acidity as determined by any of our methods and the crop yields of different soils. Oats and buckwheat in pot experiments gave good yields on soil having a total apparent acidity of 2,000 parts per million. For example, one soil with a total apparent acidity of 1,000 parts per million may not give a lower yield than a different soil having a total apparent acidity of 500 parts per million.

On the other hand, so far as our experiments have gone, the same soil having different degrees of acidity gives relatively different yields. We are not prepared to say, however, how close the agreement between crop yields and acidity is; indeed, in farm practice a close agreement is not expected. Numerous field experiments have shown, however, that even soils with as low an acidity as 400 to 600 parts per million (due almost entirely to insoluble organic acids and to absorption by nonacid materials) will not produce red clover in regular farm practice until limed. This is well shown by the Maryland experiments, where the acidity of the unlimed plot was and is now 600 parts per million.

What we believe to be the reasons for this lack of agreement between crop yields of different soils and their total apparent acidity have been given in the article above referred to in the Journal of the American Chemical Society.

No detailed data as to the comparative relation of alkaline and acid soils to water and mechanical condition can be given. In a general way it may be said that the water requirements of the plants were less on acid soil than on alkaline soils, that the former were constantly wetter, with a tendency to water-logging in the lower layer. It was a frequent observation of Mr. E. F. Smith, in charge of the laboratory of plant pathology, Bureau of Plant Industry, who made a careful examination of these bean plants, that those grown on the acid soils (unknown to him) appeared to have suffered from over-watering. The black humus sand which has been used for the past two years in a study of methods for determining acidity has required much less water in the unneutralized samples than in the neutralized. In the former it was thoroughly water-logged, was sticky and gummy with the physical characteristics, when wet, of a heavy clay rather than of a sand. The soil in the thoroughly neutralized sample was dryer, though it had received much more water, and was in excellent tilth and condition. The roots of the red clover in the water-logged pots were short, but little branched, and decayed very rapidly after cutting the crop, while those in the neutralized but much dryer pots started to grow again, and were thoroughly healthy, completely filling the pots. But one nodule was found on the roots of plants grown in the soils not completely neutralized. They were plentiful on the plants grown in alkaline soil. It is not concluded, however, that nitrogen-fixing bacteria do not develop in acid soil, only that they do not develop so well.

It should be remembered in connection with these facts that this soil has a water-soluble acidity of less than 100 parts per million, 250 parts per million by the sodium chlorid method, and a total apparent acidity of 4,000 parts per million. That is, the acidity of the soil is due almost exclusively to insoluble organic acids and nonacid organic materials.

We have but little definite data on the lasting effect of lime. One field limed at the rate of 1,000 parts per million in 1896 when it required 600 parts, was still alkaline in the summer of 1903; another field limed at the rate of 1,000 parts per million in 1900 when it required 600 parts, was still alkaline in 1903. At the Maryland station, where the soil has an acidity of 600 parts per million, the plots limed with 540, and 1,080 parts per million (calculated to a depth of 6 inches) were again acid in the fall of 1903, the first 500, the second 300 parts per million. The plot which received 1,620 parts per million was just about neutral, and the plot which received 2,140 parts was still alkaline. In other words, 1,000 parts per million of extra lime applied in 1896 had been neutralized in seven years. These results are at variance with those obtained on the fields of private farms, but as all the data are more exact the results are doubtless more accurate.

An attempt was also made to determine in a practical way the speed with which applied lime neutralizes the acids of the subsoil. To obtain these data quickly, and to give them practical significance, in the summer of 1903 the writer took samples from about 60 fields in localities where liming has been more or less the general practice for the last 20 years. With many of these fields from which samples were drawn the writer has a personal acquaintance covering that period. Samples were drawn from the limed fields and for comparison from the old fence rows around them or from contiguous woodland. The soils examined embraced those derived from hydromica schists, from granite, from triassic red sandstones, Heldeberg limestone, and from the heavy clays and various loams of the Coastal Plain.

Although some of the fields examined had received as much as 150 bushels of burned stone lime per acre in the last 20 years, and have often been plowed 8 to 9 inches deep, lime as carbonate, bicarbonate, or hydrate has not penetrated deeper than 12 inches. A medium loam, limed on the surface only, at the rate of 100 bushels of lime per acre, had not been reduced in acidity below one-half inch from the surface. In cooperative experiments with the Maryland station sufficient lime was applied to the plowed land in the spring of 1903, before planting corn, to neutralize the total apparent acidity of the soil to a depth of 9 inches. This lime received such incorporation with the soil as could be had in the regular operation of preparing the soil for corn and its subsequent cultivation. By the spring of 1904 the soil was still acid in the fourth inch. On the lime plots of the Maryland station, limed only in 1896, the lime has in no case neutralized the soil below the ninth inch.

From this mass of evidence the conclusion seems warranted that for practical farm purposes the neutralizing effect of applied lime is not exerted below the depth to which it is incorporated with the soil during the various processes of preparation and cultivation. Consequently, the more thorough and the deeper these operations are, the better the distribution and the more effective the action of the lime.

The knowledge thus obtained on these points enables us to say that the incorporation of lime with 3 or 4 inches of surface soil is sufficient to produce marked effects on acid soils, and also that at any one time it is needless and possibly occasionally harmful, so far as the immediately succeeding crops are concerned, to apply more lime than will neutralize the soil to a depth to which it is to be cultivated. It is the better farm practice, therefore, to apply only this amount of lime, and immediately after the next plowing to repeat the application and work it in.

These results indicate that alkaline soils are more fertile than acid soils, and produce crops more economically than acid soils do; that in applying lime the soil should finally be made alkaline to the full plowed depth; that in ordinary farm practice the acids of the subsoil are not neutralized by applied lime.

THE ESTIMATION OF SMALL QUANTITIES OF PHOSPHORIC ACID BY THE VOLUMETRIC METHOD.

By F. P. Veitch.

Having occasion recently to estimate very carefully the phosphoric acid in drainage waters and water extracts of soils, it appeared advisable to investigate certain features of the method used when such small quantities are subjected to absorption by filter paper and to other losses of manipulation. For this purpose a practically chemically pure (over 99 per cent) sodium phosphate was used, 0.5045 grams being dissolved and diluted to 1 liter, making a solution 1 cc of which contained 0.1 milligram of phosphoric acid. Phosphoric acid was determined directly in various quantities of this solution by the well-known volumetric molybdate method,[a] using standard solutions, 1 cc of which equaled 0.0005 gram of phosphoric acid. The results obtained were:

P_2O_5 taken.	P_2O_5 determined.
Mg.	*Mg.*
0.1	0.15
.1	.15
.5	.50
.5	.55
1.0	1.00
1.0	1.00

Only in the cases where 0.1 milligram of phosphoric acid was taken can the results be criticised.

Quantities of the phosphate solution were diluted to 800 cc, magnesia added, and the whole evaporated to dryness twice in the presence of nitric acid, and the residue taken up in nitric acid, and the determination made as before:

P_2O_5 taken.	P_2O_5 determined.
mg.	*mg.*
0.5	0.5
.5	.5
1.0	1.0
1.0	1.025

Portions of the phosphate solution were diluted to 1,000 cc, filtered through double filters, the first 100 cc of filtrate rejected and 800 cc of the remainder evaporated, and phosphoric acid determined as in the preceding experiment.

P_2O_5 taken.	P_2O_5 determined.
mg.	*mg.*
2.0	1.95
2.0	2.025

From these results it appears that accurate results can be obtained on such small quantities of phosphoric acid as exist in drainage waters and water extracts of soils, neither evaporation nor filtration appearing to affect the results seriously. The determinations can be completed within 2 working days.

[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bull. 46, p. 13.

[Another paper, entitled "The Estimation of Potash in Soils, Plants, and Fertilizers," was submitted by Mr. Veitch by title and may be found in the Journal of the American Chemical Society.[a]]

Mr. WHEELER. If I understood Mr. Veitch correctly, the difference in acidity did not correspond closely with the difference in crop yield. This interested me particularly because it is just what I should expect in view of the indirect manurial action, the frequent physical improvement of soils produced by lime, and the fact that the degree of benefit thus obtained must necessarily be variable. For certain crops it is possibly necessary to have enough lime present to insure that the soil water shall give an alkaline reaction, but, if I am not mistaken, by Mr. Veitch's method more lime would be indicated as necessary than would be required to produce good crops of most kind of plants.

In our work we recognize the merits of the Veitch method for certain purposes, but I wish merely to prevent the exaggeration of the idea that every soil must be limed to the extent indicated by that method before satisfactory yields of most crops can be obtained. I am also very much interested in the statement that lime does not neutralize much below the point at which it is worked in, for in the renovation of "Hoch-moor" soils by the station at Bremen it became necessary to introduce lime into the subsoil as well as into the surface layer, and for this purpose a subsoil plow, with a hopper for carrying the lime, is used, which has a set of knives in the rear to mix the lime and soil.

It should perhaps be stated here that the influence of the chemical reaction of the soil has been too generally overlooked by investigators, except in the case of water-culture work. Brooks, in summarizing certain work of the Massachusetts station, remarks that it has been found that muriate of potash should not be used in conjunction with sulphate of ammonia, or ammonium chlorid, a "poisonous" substance, will be formed. Nevertheless it has been used in England successfully as a manure, and it has been shown by the Rhode Island station to be a very effective manurial substance when the acid condition of the soil has been corrected.

A number of years ago the association was working with soils which showed certain definite soil deficiencies, but after the correction of their acidity the same deficiencies no longer existed. In this connection I would call attention to an article in the Seventeenth Annual Report of the Rhode Island Experiment Station on "Magnesia as a manure," in which certain work by Loew, May, and Kearney and Cameron is discussed. Loew calls attention to the fact, previously observed, that magnesia is sometimes poisonous in its action upon higher plants, in the absence of lime, and he advances a theory

[a] J. Amer. Chem. Soc., 1905, *27*: 56.

whereby he would explain *how* this action may be overcome by applying sufficient lime. In fact, however, some of the observations which he cites in support of his theory are more readily explained by the chemical reaction which the substances applied bring about in the soil. More recently May found that plants died where calcium and magnesium carbonates were used, but when calcium sulphate was added thereto they did not die. He attributed this solely to the greater solubility of the lime in the calcium sulphate, regardless of its action upon soluble magnesium carbonate and the changed reaction of the medium thus brought about. Kearney and Cameron also conducted experiments with magnesium carbonate in which, when they added an excess of carbon dioxid so that no hydroxyl reaction with phenolphthalein was obtainable, a strong toxic action upon the plants resulted. This they attributed to a poisonous action of the magnesia in the absence of sufficient lime. In the case of a like result with calcium carbonate they offer no explanation. They do not mention nor appear to take into account that when carbon dioxid is added in the presence of magnesium or calcium carbonate the alkalinity of the solution is very much increased, and that this is doubtless greater with magnesium than with calcium carbonate. It appears as though they had neglected the effect of this chemical reaction upon the growth of the plants.

These are but a few of the many similar instances in which in pot and field experiments this factor of the soil reaction has been too little recognized, just as it was in P. Wagner's soda experiments and in the discussion of the data cited in their support (Die Stickstoffdüngung).

Mr. Veitch. Crop yields on different soils did not correspond with the differences in the acidity of the soil, but on the same soil, having different degrees of acidity, the yield of the crops grown varied approximately with the acidity, the largest crops being obtained on the soils which had been made alkaline. If by having "enough lime present to insure that the soil water shall give a lime reaction," Mr. Wheeler means an alkaline reaction, I fully agree with him. I believe that the soil water should always contain lime as bicarbonate, and it is the amount of lime which must be applied to a soil to insure this condition which is determined approximately by the limewater method.

With regard to the necessity of completely neutralizing the soil we fully recognize that different plants offer varying degrees of resistance to acidity. For instance, oats and corn are very resistant to acids and you will get a good crop of either one where you can not grow alfalfa or red clover. If you are going to farm for fifty years it seems to me it would be wiser to have your soil neutralized—to have it slightly alkaline, rather than to have it slightly acid. It is generally recognized as the better farm practice to grow a variety of crops and get

the full benefit of those legumes which are particularly sensitive to acids.

Mr. Hopkins. It should be borne in mind that not only a physical but a chemical change is produced in the soil by the use of caustic lime. It is very difficult to determine just what action is produced in specific cases. Caustic lime has power to decompose organic matter and to act upon the mineral constituents of the soil and thus to liberate plant food from the soil. Apply caustic lime to a given soil and a marked effect on the crop is obtained—use potassium on the same soil and you also get good results, or, if not potassium, then phosphorus produces the beneficial effect, or even nitrogen applied to some soils may produce effects on crop yields similar to those produced by caustic lime. It is a question whether we should use caustic lime to force the soil to give up any element of fertility and it seems to me there is danger that the use of caustic lime will be recommended too freely as a remedy for all soil evils. There is a German proverb to the effect that "Lime may enrich the fathers, but it impoverishes the children."

Mr. Wiley. Perhaps the form in which the lime is added has something to do with this problem. Is it necessary to add caustic lime? Would it not be better to add the carbonate directly if it can be economically obtained? I have closely observed the soils of different countries and it seems to me that none retain their fertility better than the limed soils of England where chalk has been used. In the north of France also you will find great pits out of which it is said the Romans dug the chalk and scattered it on the near-by fields where lime was less abundant. I do not admit that the use of lime will "make the child poor." It may be in some cases when lime has been used that the crops have not been judiciously rotated and the supplies of nitrogen, phosphoric acid, and potash may have been exhausted, but this would be due to unscientific farming and not to the use of lime.

Mr. Hopkins. There are many mills that reduce ordinary calcium carbonate to a fine powder, but transportation must be considered in deciding what calcium compound shall be used. By adding caustic lime larger crops are produced for a few years, but the fertility of the soil is rapidly reduced. If more phosphorus is needed, is it not better to buy it rather than to force out what there is in the soil by the use of caustic lime? I think the principal use of lime should be to build up our soils, not to run them down. The chief benefit of lime on red clover is that it corrects the acidity of the soil and thus encourages the growth of the nitrogen-gathering bacteria, but this effect is produced by ground limestone as well as by caustic lime. For about twenty years the Pennsylvania station has carried on experiments with caustic lime and calcium carbonate. After sixteen years some very thorough examinations were made of these soils, the organic matter and the nitrogen were both determined, and, based upon either of these constituents,

the loss sustained by the soils treated with caustic lime was equivalent to 2 tons of farmyard manure per acre per annum—the soil so treated being that much inferior to the soil treated with calcium carbonate. It is true, of course, that caustic lime will correct the acidity of the soil and thus encourage the growth of legumes, and if plenty of legumes are grown and liberal use is made of farm manures and other plant-food materials when necessary the soil can actually be built up in productive capacity, even though caustic lime be used. I admit that it is better to use caustic lime than no lime on acid soils; but it seems to me that the beneficial effect of caustic lime—namely, the correction of soil acidity—can also be produced by the use of ground limestone, which is much cheaper to obtain in our State and which is certainly not so disagreeable to handle as caustic lime. It seems unnecessary, if not absurd, to burn the limestone to make caustic lime and thus "burn" the organic matter out of our soils to a greater or less extent, instead of using finely ground limestone itself, which produces the benefits without any injurious effects.

Mr. Veitch. The soil formations that have been famous for thousands of years for their fertility are alkaline in reaction. The adding of lime to such soils is not advisable, as we see from the results of the Pennsylvania station, where the soil is a magnesium limestone. I have had life experience in a region which owes its present fertility to the use of caustic lime. Twenty years ago there was no lime used in this section of Maryland, and the land was getting very poor even though fertilizers were extensively used. The lands have now been built up by the judicious use of lime in connection with other fertilizers so that they are now fertile. We are, of course, familiar with the fact that lime has other effects than that of simply neutralizing acids and these effects have been shown in the paper submitted, in the greater solubility and availability of all the essential constituents, as well as in the lower activity of fungi and the improved physical condition of the soils. But, to use Mr. Hopkins's argument, may not some of the benefit derived from the use of potash salts be due to the lime brought into solution thereby? I do not agree with Mr. Hopkins that the use of lime, where needed, reduces the fertility. My experience and observation has been that with good farming the use of lime increases or more easily maintains fertility. Nor can I agree that the chief benefit of lime is in encouraging the growth of nitrogen-fixing bacteria, beneficial as it undoubtedly is in this particular. So far our experiments and observations indicate that the root of red clover is more sensitive to acids than the bacteria are; that is, the bacteria are still alive in soil which will not grow clover until limed, even though an abundance of nitrates is present.

At the close of the discussion on the liming of soils the morning session adjourned.

TUESDAY—AFTERNOON SESSION.

At the opening of the afternoon session the report on tannin was presented by the referee.

REPORT ON TANNIN.

By G. A. Kerr, *Referee.*

In accordance with the conclusions drawn from last year's work and the suggestions made by the referee, the following lines of work were taken up this year and investigations pursued with more than ordinary interest.

(I) The analyses of chestnut, quebracho, and hemlock extracts by the present provisional method. This work was sent out for the purpose of securing a basis of comparison for the special work.

(II) A special study with a view of ascertaining the causes of variation in soluble solids and insoluble matter found in extracts.

(III) The analyses of fresh and leached bark and fresh chestnut wood, according to the laboratory method of each individual collaborator. The referee, being aware of the lack of uniformity in the results returned by different analysts and consequent dissatisfaction among manufacturers employing the services of chemists, considered it advisable to ascertain the status of this particular branch of tannin determination in order that such faults as might be found to exist could be corrected and a method which would yield more uniform results and greater accuracy developed.

(IV) The further investigation of the provisional methods for determination of acid (acetic and lactic) in yard liquors.

(V) A further test to confirm the recommendations made last year regarding the necessity of protecting solutions during manipulation against changes caused by evaporation.

Study I. Comparative Work with the so-called Official Method.[a]

Comparing the relative difference in results contained in Tables I–III, analyses of chestnut, hemlock, and quebracho extracts, it seems that in the case of chestnut extract alone the present association method comes within the limit of acceptance.

The results returned on the hemlock and quebracho extracts, though an improvement over previous years, still leave much to be desired in the line of accuracy, especially regarding the items of solubles and insolubles. The nontannin figure, which previous to the adoption of chromed hidepowder was the greatest source of error, is now the most uniform, and, excepting instances where faulty manipulation is obvious, or variations clearly traceable to other sources interfere, the results on this item, herewith submitted, confirm previous work relative to the value of chromed hidepowder.

[a] [Note by the Editor.—This method, being the one exclusively used by the association for tannin determinations, has come to be known as "official," but it has never been formally adopted by the association as such, as was explained in the report of the proceedings of the nineteenth convention (Bureau of Chemistry, Bul. 73, pp. 174–175). The editor has therefore corrected this report to read "provisional" or "association" method in referring to the tannin method given in Bul. 46.]

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TABLE I.—*Analysis of chestnut-wood extract, by provisional method.*

Analyst.	Total solids.	Soluble solids.	Insolubles.	Nontannins.	Tannins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
H. C. Reed	37.40	37.05	0.35	10.90	26.15
W. K. Alsop	37.28	36.94	.34	10.59	26.35
Yocum Manufacturing Co., C. Eachus	38.14	37.61	.53	11.38	26.23
Fritz H. Small	37.63	36.84	.79	10.97	25.87
H. T. Wilson	37.50	36.93	.57	11.13	25.80
W. H. Teas	37.84	37.09	.75	11.28	25.81
H. Gerber	38.17	37.97	.20	[a] 12.23	[a] 25.74
J. C. Scott	38.50	38.08	.42	[a] 13.12	[a] 24.96
A. J. Stillwell	37.73	36.62	1.11	11.61	25.01
C. W. Norris	37.72	37.04	.68	11.01	26.03
F. M. Loveland	38.20	37.39	.81	[a] 12.69	[a] 24.70
E. R. McCarthy	37.41	36.47	.94	11.10	25.37
Average	37.79	37.17	.624	11.108	25.85
Maximum	38.50	38.08	1.11	11.61	26.35
Minimum	37.28	36.47	.20	10.59	25.01
Greatest difference	1.22	1.61	.91	1.02	1.34
Greatest variation from average	.71	.91	.487	.518	.84

[a] Omitted from average, as error is obvious.

TABLE II.—*Analysis of hemlock extract, by provisional method.*

Analyst.	Total solids.	Soluble solids.	Insolubles.	Nontannins.	Tannins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
H. C. Reed	45.40	43.48	1.92	15.01	28.47
W. K. Alsop	45.39	43.25	2.14	14.39	28.86
Yocum Manufacturing Co., C. Eachus	45.90	42.84	3.06	13.92	28.92
Fritz H. Small	45.64	40.86	4.78	14.17	26.69
H. T. Wilson	45.58	42.80	2.78	14.76	28.04
W. H. Teas	45.92	41.08	4.84	15.02	26.06
Harry Gerber	45.29	42.86	2.43	[a] 16.90	[a] 25.96
J. C. Scott	46.56	44.16	2.40	[a] 17.70	[a] 26.46
A. J. Stillwell	44.61	41.63	2.98	15.52	26.11
C. W. Norris	45.53	42.00	3.53	15.64	26.36
F. M. Loveland	46.18	43.81	2.37	[a] 17.56	[a] 26.25
E. R. McCarthy	45.92	43.99	1.93	14.06	29.93
Average	45.66	42.73	2.93	14.72	27.71
Maximum	46.56	44.16	4.84	15.64	29.93
Minimum	44.61	40.86	1.92	13.92	26.06
Greatest difference	1.95	3.30	2.92	1.92	3.87
Greatest variation from average	1.05	1.87	1.91	.92	2.22

[a] Excluded from average on account of obvious error.

TABLE III.—*Analysis of quebracho extract, by provisional method.*

Analyst.	Total solids.	Soluble solids.	Insolubles.	Nontannins.	Tannins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
H. C. Reed	50.31	47.68	2.63	8.54	39.14
W. K. Alsop	50.39	47.65	2.74	8.67	38.98
Yocum Manufacturing Co., C. Eachus	50.63	48.00	2.63	8.67	39.33
H. T. Wilson	50.33	48.11	2.22	8.56	39.55
Fritz H. Small	50.30	47.14	3.16	8.29	38.85
W. H. Teas	50.98	47.59	3.39	8.69	38.90
Harry Gerber	50.23	49.03	[a] 1.20	[a] 11.92	[a] 37.11
E. R. McCarthy	51.03	48.85	2.18	8.95	39.90
J. C. Scott	51.45	48.73	2.72	10.14	38.59
A. J. Stillwell	51.92	[a] 51.11	[a] .81	10.85	40.26
C. W. Norris	51.20	48.80	2.40	8.84	39.96
F. M. Loveland	51.90	48.79	3.11	9.65	39.14
Average	50.89	48.21	2.71	9.08	39.33
Maximum	51.92	49.03	3.39	10.85	40.26
Minimum	50.23	47.14	2.18	8.29	38.59
Greatest difference	1.69	1.89	1.21	2.56	1.67
Greatest variation from average	1.03	1.07	.68	1.77	.93

[a] Excluded from average on account of obvious error.

STUDY II. SOLUBLE SOLIDS AND INSOLUBLES.

Previous reports having made obvious the necessity for greater uniformity in the results on soluble solids and insolubles which have a direct bearing upon the tannin figure and have shown little tendency toward permanent improvement, the referee appointed a special committee for research along this line, the members of which were Messrs. F. H. Small, H. T. Wilson, and H. C. Reed.

Mr. Small first called the referee's attention to a variation he had found to exist in his laboratory in the soluble solid and insoluble figures obtained when analyses were conducted at different temperatures, and submitted results obtained on the official samples of extracts sent out this year. These figures are given below for comparison with results of analyses given under Study I:

TABLE IV.—*Analyses of official samples of extract by Mr. Small, illustrating the difference in results, presumably caused by variation in laboratory temperature.*

Determinations.	Chestnut extract.		Hemlock extract.		Quebracho extract.	
	20° C.	25° C.	20° C.	25° C.	20° C.	25° C.
Total solids	37.63	37.55	45.64	45.58	50.30	50.34
Soluble solids	36.84	36.85	40.86	42.93	47.14	48.48
Insolubles	.79	.70	4.78	2.65	3.16	1.86
Nontannins	10.97	10.85	14.17	14.45	8.29	8.51
Tannins	25.87	26.00	26.69	28.48	38.85	39.97

Mr. Small remarks in the case of hemlock at 25° C that the filtered solution was not quite clear. Knowing it had been previously observed that variations were caused by differences in temperature, the referee looked for results of previous research, but was unable to find any figures which indicated the considerable extent of the variation within the limited range of temperature shown by Mr. Small's results. Considering the suggestion thus given of much interest and probable value, the referee decided to submit the question to a committee for confirmation. The

results returned by the members confirm Mr. Small's figures in a general way, and prove conclusively that some limitation in temperature must be defined to secure uniformity. In order to test the question, samples of hemlock and quebracho extracts were sent to the committee with the request that the soluble solids and insolubles be determined at 15°, 20°, 25°, and 30° C, respectively. From the tables of results which follow it will be seen that in both cases a constant increase in temperature yields higher solubles and lower insolubles. The average decrease of insolubles at an increase of 15° C in the case of the hemlock being 2.02 or 48 per cent of the quantity found at 15°, and in the case of quebracho 1.5 or 37 per cent of the quantity found at 15° C, while a practically corresponding increase in the solubles is found. It need scarcely be suggested that under like circumstances the tannin figure will necessarily follow a similar variation.

TABLE V.—*Effect of variations in temperature on determination of soluble solids and insolubles in hemlock extract.*

Analyst.	Total solids.				Soluble solids.				Insolubles.			
	15° C.	20° C.	25° C.	30° C.	15° C.	20° C.	25° C.	30° C.	15° C.	20° C.	25° C.	30° C.
	Perct.	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*
H. T. Wilson	45.80	45.92	45.62	45.78	41.44	42.28	43.14	43.93	4.36	3.64	2.48	1.85
H. C. Reed	45.99	45.99	45.99	45.99	42.19	43.48	43.65	44.22	3.08	2.51	2.34	1.77
F. A. Small	45.89	45.94	45.91	45.94	40.63	41.49	42.44	42.94	5.26	4.45	3.47	3.00
Average	45.89	45.95	45 84	45.90	41.42	42.42	43.08	43.69	4.23	3.53	2.76	2.21

The average difference in soluble solids for each 5° of temperature from 15° to 30° C is shown to be as follows: Between 15° and 20°, 1 per cent; between 20° and 25°, 0.66 per cent, and between 25° and 30°, 0.61 per cent. The total soluble solids are constantly increasing with rising temperature. The total average difference in soluble solids between 15° and 30° C is 2.27 per cent, while the average difference in insolubles for 5° of temperature is, between 15° and 20°, 0.7 per cent; between 20° and 25°, 0.77 per cent, and between 25° and 30°, 0.55 per cent. The insolubles are constantly decreasing with rising temperature. The total average difference in insolubles between 15° and 30° C is 2.02 per cent.

TABLE VI.—*Effect of variations in temperature on determination of soluble solids and insolubles in quebracho extract.*

Analyst.	Total solids.				Soluble solids.				Insolubles.			
	15° C.	20° C.	25° C.	30° C.	15° C.	20° C.	25° C.	30° C.	15° C.	20° C.	25° C.	30° C.
	Perct.	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*	*Perct.*
H. T. Wilson	51.13	51.12	51.14	51.25	47.22	47.15	47.45	48.48	3.91	3.97	3.69	2.77
H. C. Reed	50.50	50.50	50.50	50.50	46.55	47.19	47.27	47.86	3.95	3.31	3.23	2.64
F. A. Small	51.23	50.76	50.66	50.75	46.28	47.42	47.76	48.09	4.95	3.34	2.90	2.66
Average	50.95	50.79	50.76	50.83	46.68	47.25	47.49	48.14	4.27	3.54	3.27	2.69

The average difference in soluble solids for each 5° of temperature from 15° to 30° C, as shown in Table VI, is as follows: Between 15° and 20°, 0.57 per cent; between 20° and 25°, 0.24 per cent; between 25° and 30°, 0.65 per cent—a constant increase. The total average increase in soluble solids between 15° and 30° C is 1.46 per cent. The average decrease in insolubles for 5° of temperature is, between 15° and 20°, 0.73 per cent; between 20° and 25°, 0.27 per cent, and between 25° and 30°, 0.58 per cent—

a constant decrease. The total decrease in insolubles between 15° and 30° is 1.58 per cent.

The results of the tests made this year must not be considered regarding uniformity, as the work was done during weather conditions which made it extremely difficult to maintain the desired temperatures. They, however, accord sufficiently in a general way to show that the subject is worthy of further investigation, and the referee would earnestly suggest that further experiments be conducted during the coming year, with a view of ascertaining the behavior of tannin solutions under various conditions. The work, in his opinion, should include experiments to determine the most favorable temperature at which the solution of various tanning materials should be analyzed; means of maintaining such temperature; the effect of cooling and reheating solutions; the effect of varying temperatures of water used for dilution, and the solubility of the reds or phlobaphens of various tanning materials in relation to temperature.

In order to ascertain, if possible, the probabilities of error arising from this source in laboratories located so far apart as to be working almost continuously under widely differing conditions, the referee sent cards to 16 laboratories requesting a return of the summer and winter temperatures prevailing during working hours. From the figures given below the reader will note that maximum summer temperatures vary 16° C and the minimum 9° C, while the maximum winter temperatures vary 7° and the minimum 16.5°. With these figures as a basis, it appears reasonable to assume that such differences in temperature to a great extent account for the lack of uniformity existing.

TABLE VII.—*Variations in laboratory temperatures.*

Location.	Summer temperature.		Winter temperature.	
	Maximum.	Minimum.	Maximum.	Minimum.
	° *C.*	° *C.*	° *C.*	° *C.*
Huntsville, Ontario	27.2	21.1	23.8	15.5
Milwaukee, Wis	36.0	18.0	28.0	10.0
Fremont, Mich	29.0	.....	.....	15.0
Worcester, Mass	34.0	15.0	27.0	10.0
Stamford, Conn	32.0	24.0	25.0	20.5
Lockhaven, Pa	32.0	21.0	24.0	13.0
Ridgeway, Pa	43.0	18.0	27.0	4.4
Newark, N. J	34.4	23.3	23.8	18.3
Chicago, Ill	27.0	18.0	21.0	15.0
Buena Vista, Va	38.0	20.0	21.0	21.0
Damascus, Va	36.0	20.0	26.0	15.0

COLLABORATORS' NOTES ON STUDY II.

Mr. Small.—My results confirm Mr. Wilson's in a general way, though there is no very exact agreement. My laboratory temperature was over 30° C at one time, which made it very difficult to keep liquors at a constant temperature of 15° C for the several hours required for the filtrations. I presume had we been better equipped for the work, and had the temperature conditions been more favorable, the results might have run somewhat closer. There certainly seems to be no question but that the temperature feature is an important one, and work on soluble solids should be done within as limited a range as possible.

Mr. Wilson.—I think that cognizance should be taken of the variations shown by temperature tests, but of course it is impossible to arrive at any definite figures for correction purposes from the limited amount of work done so far, and this work should be carried over for another year, being done during the winter months, when it will be much easier to govern the temperature. Probably there will not be much

change on chestnut extract, but the large variations in hemlock indicate the need of closer control of temperature. I suppose any extract rich in reds will show wide variations. * * * All filtrations were made in funnels surrounded by water jackets 2 inches thick, in which water of desired temperature was constantly kept by replenishing from a larger reservoir of like temperature. Temperatures did not vary more than 1° in the water jacket, except in case of quebracho at 15°. Filtrations at low temperatures were extremely slow. Receptacles for filtrates were kept corked according to the recommendation in previous instructions.

Mr. Reed.—Looking at the results from any standpoint, it is evident that the temperature in filtration has considerable to do with the resulting soluble solids, but before recommending that the solutions be filtered at certain temperatures, I would suggest that we consider the effect of cooling the solutions to a fixed temperature, permitting them to return to room temperature, filtering and noting whether under these circumstances the resulting soluble solids will not be practically uniform. I think that if the solution is cooled to about 20° C and the temperature allowed to rise to that of the laboratory (provided of course that the temperature must rise in order to come to that of the room) the insolubles would not again return to solution. You will observe that my results on the quebracho show but slight differences on soluble solids between 20° and 25°, and I note that Mr. Wilson's results show the same thing.

Study III. Analyses of Barks and Wood.

Twelve analysts participated in this section of the work, and the tabulation of their results shows just that many variations in the course of procedure at one or more of the important stages of the analyses.

Reviewing the tables and beginning with the analyses it is apparent that in the case of the three first items (total solids, soluble solids, and insolubles) the chief source of difference is attributable to one or more of the following causes: The preparation of the material to be analyzed before extraction, the conditions under which extraction is conducted, the degree of extraction practiced, the quantity of material used, the volume of water employed, or the method and extent of dilution after extraction is completed.

The next item, nontannins, as in the case of extracts, shows greater uniformity, though the difference, relative to the total percentage of soluble solids, is out of all proportion. Referring to Table I, it will be seen that the greatest difference in the average nontannins found in the official sample of hemlock extract is only about 6 per cent of the whole, whereas in the leached hemlock bark it is 30 per cent. The error is greater in the case of the ultimate figure, tannin, this being accounted for by the differences in the second and third items.

Leaving the results and taking up the data relative to methods, the referee calls attention to the remarkable variations in the quantity of material used for extraction, and the soluble extractive contents of the final dilution, ranging in the case of spent bark from 0.106 gram to 0.6764 gram per 100 cc of solution. The difference is not quite so great in the case of fresh hemlock bark and fresh chestnut wood, but it is not quite clear that it is altogether customary to be governed in detail by the provisional method, especially in the analysis of spent materials. There is in several instances an apparent lack of attention to the requirements. This point, however, is not without its value, as it tends to demonstrate the stability of the powder as now prepared.

The majority of the analysts used the automatic syphon Soxhlet extractor, two, a percolation method, one, the regular Soxhlet, one, the Proctor method, and one, not specified. The time of extraction ranged from 8 to 16 hours.

Summing up the results, it is evident that a more detailed method covering preparation of material, quantity of material to be used, extraction, and quantity of soluble extractions relative to volume is desirable. Accordingly, your referee has drawn

up the following provisional method. This is not by any means submitted as a perfected method, but rather as a basis for future investigation.

PROPOSED PROVISIONAL METHOD FOR BARKS, WOODS, LEAVES, ETC.

I. *Moisture determination.*

Immediately upon receipt of sample, grind or crush as finely as possible 25 grams and dry for 12 hours at 100° C, reweigh, and calculate difference as water.

II. *Preparation of sample for extraction.*

Barks, woods, leaves, and other tanning materials, such as nutgalls, myrobalans, etc., should be dried sufficiently to facilitate grinding and then ground to such a degree of fineness that the sample will pass through a sieve of 14 meshes to the inch (linear).

In case of a coarser residue being left after sieving, it should be reground until the entire quantity passes through the sieve. A style of grinder should be used that will make a granular preparation of the desired size, not finer. An excess of dust and very fine particles must be guarded against in order that a rapid and complete extraction may be obtained.

III. *Quantity of sample to be used for extraction.*

Such a quantity of the material to be analyzed should be taken as will yield a sufficient volume of liquor having a specific gravity of 1.0025 at 15° C. Should the gravity of the liquor prove greater than the above, dilute to the desired point with water at about 80° C. If, however, it should prove impracticable to obtain from spent material the necessary volume of liquor of the gravity specified, the gravity should be taken and the quantity of hide powder used to precipitate the tannin reduced in proportion.

IV. *Extraction of sample.*

The extraction may be carried out in any form of extractor that will give complete extraction, with a yield of not more than 1 liter of liquor. A temperature of 100° C should be maintained throughout the entire operation, except in the case of sumac and starch-bearing materials when a maximum of 80° C will be found better, and extraction continued until the resulting liquor shows no precipitation with gelatin solution, according to the provisional method for testing nontannins. Should the volume of liquor prove insufficient, dilution should be made immediately with water at 80° C to as near the mark as possible.

In case of pulverized or finely ground material, such as sumac, powdered nutgalls, etc., the extraction will be materially assisted by thoroughly mixing the sample with glass sand free from iron and matter precipitable or soluble in hot tannin solution.

V. *Total solids.*

After extraction and final dilution cool slowly to about 20° C, shake thoroughly, allow to stand for one hour, then pipette 100 cc into a tared dish, evaporate, dry, and weigh according to the provisional method.

VI. *Soluble solids, nontannins, and tannin.*

The determination of these constituents should be conducted by the provisional method.

In all cases it is best to conduct the analyses on a dry basis; that is, with the material dried at 100° C. If the analysis is made to determine the tanning or commercial value, results should be calculated back to the natural condition of the material. In the case of analyses made for comparison between fresh and spent materials, and

in controlling tannery or extract manufacturing processes, results are more conveniently calculated and recorded on a dry basis.

Attention must be given to the quantity of hide powder used in determining nontannins. See Paragraph III, Quantity of sample, etc., above.

Some changes from the usual course of procedure in analyzing crude tanning materials have been made in the method given. In Paragraph I, 25 grams have been specified as requisite for moisture determination, as a smaller quantity can scarcely under any conditions be made representative of the quantity of material involved in the analyses. A sample usually represents the contents of a leach or carload, and not infrequently a considerable portion of a cargo; it will therefore be appreciated that in the case of crude tanning materials it is difficult to procure a truly representative sample, and in the majority of instances it is easy to secure a sufficient quantity of the material to be analyzed to permit the use of at least 25 grams.

Regarding Paragraph II, Preparation of sample for extraction, it is doubtless true that an extraction can not be completed any quicker than the largest particle of the material will yield its extractives. As a rapid and complete extraction is desirable in order to obviate an unnecessarily prolonged boiling of the resulting extractives, such as they are subjected to in the case of the Soxhlet extractor, the value of having a uniform preparation and one limited as to the size of the largest particles is apparent, and will probably cover the question of time limit for extraction.

As to Paragraph III, Quantity of sample to be used for extraction, reference to the table covering barks and woods will reveal a great variation on this point, and from any standpoint it is a difficult problem to solve. Considering the question superficially, it would seem there should be no difficulty in compiling a table of quantities embracing the various kinds of crude materials, based upon the quantity of tannin per 100 cc specified in the provisional method. That this would prove practical is probably true in the case of certain classes of tannin-bearing products, but for our domestic materials, and in the case of spent or leached materials, it seems hardly adaptable.

Your referee instead of specifying a given quantity suggests for the present, and not as altogether a solution of the question, that the liquors resulting from extraction be restricted as nearly as possible to a specific gravity of 1.0025, which will yield with sufficient constancy the quantity of tannin which comes within the limit specified by the provisional method. In this way it may be possible to attain a certain degree of uniformity, as the only precaution necessary is to use a sufficiency of the material analyzed, restricting the volume, of course, within reason. After a little experience, the strength of solution could be kept on the safe side; that is, a little greater than the gravity specified, and regulated by dilution.

A more important advantage to be obtained by governing the strength of these solutions by gravity is that by this means the proper quantity of hide powder can be readily estimated. By referring to the table it will be seen that the quantity used varies from 9.24 to 17.2 grams. In most cases it is apparent that some effort has been made to base the quantity upon the tannin contents of the solution, but with one or two exceptions the quantity relative to the tannin contents as laid down by the present provisional method is inaccurate.

Paragraph IV, Extraction of sample, does not materially change existing methods of procedure, and is designed merely to govern further test work until the efficiency of the various methods of extraction is demonstrated.

Total solids, Paragraph V, while not absolutely essential for a determination of tanning value, has its uses in several industries, and it will further serve in studying the effect of the Soxhlet and other extractors upon the liquors of extraction.

Soluble solids, nontannins, and tannins, Paragraph VI, assuming that the foregoing items yield to the analyst a liquor in accordance with the provisional method, should be determined in strict accordance with the same.

TABLE VIII.—*Analyses of fresh hemlock bark (dried at 100° C).*

Analyst.	Extractives.			Nontannin.	Tannin.	Amount of bark used.	Volume of liquor.		Strength of solution.	Duration of extraction.	Method of extraction.	Dry hide powder per 200 cc.
	Total.	Soluble.	Insoluble.				Obtained.	Made up to.				
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Gms.*	*cc.*	*cc.*	*Grams per 100 cc.*	*Hrs.*		*Gms.*
H. C. R	21.34	18.77	2.57	5.98	12.79	35	800	1,000	0.6569	10	Siphon Soxhlet.	12.8
W. K. A	22.13	19.65	2.48	6.60	13.05	25	800	1,000	.496	10	.....do.....	9.8
Yocum, C. E	20.13	17.45	2.68	6.30	11.15	25	.....	1,000	.4362	9	.....do.....	10.0
F. H. S	22.11	19.03	3.08	6.01	13.02	18	500	500	.6850	9	.....do.....	15.0
H. T. W	25.11	19.12	5.99	6.61	12.51	35	900	1,000	.669	12	.....do.....	14.87
W. H. T	21.96	17.98	3.98	6.43	11.55	25	900	1,000	.494	10	.....do.....	10.00
H. G	.....	12.50	.....	4.41	8.09	16	625	1,000	.2002	8	....	13.5
E. R. McC	21.07	18.79	2.28	4.34	14.45	25	900	900	.522	8	Percolation	13.5
J. C. S	.....	19.49	.....	6.44	13.05	25	1,000	1,000	.487	.....	.....do.....	14.27
C. W. N	21.19	18.99	2.20	6.36	12.63	30	750	.....	.5697	8	Siphon Soxhlet.	11.48
F. M. L	19.81	17.80	2.01	5.95	11.85	20	1,000	1,000	.256	.....	Proctor	18.78
Average	21.65	18.14	3.03	5.95	12.19	.....	.....	.....	.....	.....	.....	.....
Maximum	25.11	19.65	5.99	6.61	14.45	35	1,000	1,000	.6850	12	.....	18.78
Minimum	19.81	12.50	2.01	4.34	8.09	16	500	900	.2002	8	.....	9.80
Greatest difference.	5.30	7.15	3.98	2.27	6.36	19	500	100	.4848	4	.....	8.98
Greatest variation from average.	3.46	5.64	2.96	1.61	4.10	.....	.....	.....	.....	.....	.....	.....

TABLE IX.—*Analyses of spent hemlock bark (dried at 100° C).*

Analyst.	Extractives.			Nontannin.	Tannin.	Amount of bark used.	Volume of liquor.	Strength of solution made up.	Duration of extraction.	Method of extraction.	Dry hide powder per 200 cc.
	Total.	Soluble.	Insoluble.								
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Gms.*	*cc.*	*Grams per 100 cc.*	*Hrs.*		*Gms.*
H. C. R	6.67	6.08	0.59	3.07	3.01	50	1,000	0.304	10	Siphon Soxhlet	12.8
W. K. A	7	6.20	.80	2.95	3.25	60	1,000	.372	10	.....do.....	9.8
Yocum, C. E	7.15	6.45	.70	3.47	2.98	50	1,000	.322	9	.....do.....	10.0
F. H. S	6.35	5.64	.71	2.88	2.76	60	500	.6764	9	.....do.....	15.0
H. T. W	9.01	7.14	1.87	3.99	3.15	62	600	.559	12	.....do.....	10.8
W. H. T	6.96	6.13	.83	3.23	2.90	50	900	.3067	10	.....do.....	12.5
H. G	.....	4.03	.....	2.71	1.32	70	500	.1412	8	.....	13.5
E. R. McC	6.03	5.57	.46	2.51	3.06	50	1,000	.....	12	Percolation	11.0
J. C. S	.....	4.76	.....	2.56	2.20	60	1,000	.286	.....	.....do.....	14.27
A. J. S	6.08	5.38	.70	2.75	2.63	50	800	.3362	10	Regular Soxhlet	17.2
C. W. N	5.75	5.49	.26	2.95	2.54	65	750	.3569	8	Siphon Soxhlet	9.24
F. M. L	5.63	5.30	.33	3.76	1.54	20	1,000	.106	.....	Proctor	14.73
Average	6.66	5.68	.725	3.07	2.61	.....	.....	.....	.....	.....	.....
Maximum	9.01	7.14	1.87	3.99	3.25	70	.....	.6764	12	.....	17.2
Minimum	5.63	4.03	.26	2.51	1.32	20	.....	.1060	8	.....	9.24
Greatest difference.	3.38	3.11	1.61	1.48	1.93	50	.....	.5764	4	.....	7.96
Greatest variation from average.	2.35	1.65	1.14	.92	1.29	.....	.....	.....	.....	.....	.....

TABLE X.—*Analyses of chestnut wood (dried at 100° C).*

Analyst.	Extractives.			Nontannin.	Tannin.	Amount of wood used.	Volume of liquor.		Strength of solution.	Duration of extraction.	Method of extraction.	Dry hide powder per 200 cc.
	Total.	Soluble.	Insoluble.				Obtained.	Made up to.				
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Gms.*	*cc.*	*cc.*	*Grams per 100 cc.*	*Hrs.*		*Gms.*
H. C. R	12.01	10.64	1.37	3.59	7.05	45	800	1,000	0.4788	10	Siphon Soxhlet.	12.8
W. K. A	12.15	11.09	1.06	3.78	7.31	30	800	1,000	.3327	10	.....do.....	9.8
Yocum, C. E	12.09	11.20	.89	4.20	7	.....	.....	1,000	.280	9	.....do.....	10.0
H. T. W	14.13	12.45	1.68	5.26	7.19	45	850	.....	.562	16	.....do.....	14.87
W. H. T	11.63	9.71	1.92	3.53	6.18	50	900	1,000	.4852	10	.....do.....	10.00
H. G	.....	8.5	.....	2.30	6.20	.....	.....	.....	.....	.....	.....	.....
E. R. McC	9.70	9.01	.69	2.32	6.69	50	900	900	.500	8	Percolation .	13.5
J. C. S	.....	9.62	.....	2.91	6.71	50	1,000	.....	.481	.....	.....do.....	14.27
A. J. S	11.16	10.01	1.15	3.41	6.60	25	800	.....	.3125	10	Regular Soxhlet.	17.2
C. W. N	11.35	10.50	.85	3.52	6.98	65	750	.....	.682	8	Siphon Soxhlet.	10.6
F. M. L	9.23	8.92	.31	4.02	4.90	20	1,000	.....	.1784	.....	Proctor.....	14.61
Average	11.49	10.15	1.10	3.53	6.62	.....	.....	.....	.....	.....	.....	.....
Maximum	14.13	12.45	1.92	5.26	7.31	65	1,000	.....	.....	.....	.....	.....
Minimum	9.23	8.50	.31	2.30	4.90	20	750	.....	.....	.....	.....	.....
Greatest difference.	4.90	3.95	1.61	2.96	2.41	45	250	.....	.....	.....	.....	.....

COLLABORATORS' NOTES ON STUDY III.

H. C. Reed.—Concerning the analysis of barks, woods, etc., it appears to me advisable that the amounts of the materials to be used for extraction should be specified. * * * If we decide to adopt a method calling for a uniform weight of solids per 100 cc a table could be readily compiled on this basis. Paessler states that for spent tans 50 grams of the material should be used. I believe that many chemists are using 100 grams and am confident that this is too large a quantity. I am quite positive that it is for the extractor which I use.

Another matter in the spent tan analysis which needs consideration is the amount of hide powder to be used. I have myself been employing half as much wet hide for the spent tan analysis as is specified for the analysis of extracts, fresh barks, etc. * * * I presume that the majority of tannin chemists dry barks, woods, etc., at 100° C before extraction. It has not been my custom to do this, but to make a separate determination of the amount of water present and to calculate from this the analysis of the dry material.

Again, I believe there should be some uniform method of extraction adopted, specifying possibly the extractor to be used, although it is doubtful if a single apparatus could be used for the extraction of all tanning materials. For example, I do not believe it possible to properly extract quebracho wood by the method that Proctor uses, as it requires more drastic treatment. On the other hand, sumac and materials of this character can not be extracted in an apparatus such as is used in the United States Leather Company's laboratory and in my own. * * * I confess I do not entirely like the prolonged boiling of the tannin solution with the Soxhlet apparatus whereby the nontannins are undoubtedly increased. It would appear probable that after the limit of the extraction was reached the nontannin would go on increasing at the expense of the tannins. When we stop to consider, there are a great many

items entering into the method of laboratory extraction—for instance, the amount of heat, the length of time, and the character of material. I believe an apparatus could be designed somewhat on the principle of the Soxhlet, but with an improvement whereby a portion of the extraction—the earliest off—could be recovered and not submitted to further boiling.

H. T. Wilson.—It is customary with us to take enough spent bark to give a liquor as near official strength as possible. Sample No. 2 was too small to give liquor of such strength. Presuming the chestnut wood to be of the same strength as the usual run, we manipulated in the usual manner. The resultant liquor was below the required strength and the quantity of hide powder was higher than called for. Samples were coarser than our regular preparation, especially in the case of the wood. Time of extraction was extremely long, which was no doubt due to the sample being coarse. We extract regularly 10 to 12 hours with good results. It is our opinion that a definite quantity of material should be always taken for extraction, as results are not uniform with varying quantities. The subjoined table on spent bark will illustrate this point.

TABLE XI.—*Comparison of results obtained using varying quantities of material.*[a]

Number of sample.	Quantity of material.	Soluble solids.	Tannin.	Nontannin.
	Grams.	*Per cent.*	*Per cent.*	*Per cent.*
1	20	5.53	2.61	2.92
2	40	5.35	2.58	2.77
3	60	5.07	2.64	2.43
[b]4	.....	.....	.....	.....
5	100	4.66	2.49	2.17
6	120	4.78	2.49	2.29
7	140	4.60	2.43	2.17

[a] Made up to 100 cc for analysis.
[b] Omitted on account of incomplete extraction.

Note the almost constant tannin, while the soluble solids and nontannins decrease markedly with the increasing strength of liquor. It is our opinion that total solids and insoluble solids determinations on barks and tans are without much value. It is difficult to obtain concordant results, and the process of filtering the hot liquor from the extractor is troublesome and often tedious.

C. Eachus, Yocum Manufacturing Company.—Our method for barks is to extract 25 grams dry new bark or 50 grams dry spent bark in the copper Soxhlet extractor for nine hours, cool over night, and make up to 1,000 cc. Make total solids and soluble solids as in extracts. We use 40 grams of squeezed hide powder (chromed) for nontannins; shake 5 minutes, and finish as for extracts.

W. K. Alsop, U. S. Leather Company.—The bark and wood samples were all extracted in a copper extractor at 100° C. The solutions were made up to 1 liter, about 800 cc being obtained from the extractors. For solids the solutions were shaken and let stand half an hour, then 100 cc removed. For soluble solids 150 cc were stirred with 5 grams of kaolin, filtered off, and thrown away; the filter filled again and 100 cc collected. For nontannins 200 cc were shaken 5 minutes with 40 grams of hide powder, 5 grams kaolin added to the glass, then shaken by hand and filtered, 100 cc of clear filtrate being collected. The amount of dry hide powder used was 9.8 grams. The amounts taken for analysis, 25 grams of fresh bark, 60 grams of spent bark, and 30 grams of wood.

Wm. H. Teas, Elk Tanning Company.—The barks and woods were extracted in a modified Soxhlet extractor. Fifty grams of wood and spent bark were extracted

and 25 grams of new bark. After being weighed into an extractor cup, 1 liter of distilled water was poured on the charge and siphoned through to the reservoir. The extractor was connected up, the flame applied to the reservoir, and extraction continued for 10 hours. The solution was then allowed to cool and liquor amounting to 900 cc removed, made up to a liter, and the analysis made.

A. J. Stilwell.—Private work has convinced me that the method of extraction used by myself is either too severe or the continued boiling of the tannin solution is an error. In my opinion no automatic extractor should be allowed that will not approximately conform in results to those obtained by using the old "Proctor beaker method." The criterion of the extraction should be the soluble solids contents of the tannin solution and the time of extraction 10 to 12 hours, by agreement.

J. C. Scott.—The extractions for Study III were obtained by the use of a copper percolator with a perforated copper disk soldered in the bottom of the cylinder. Next to this cotton was pressed so as to hinder the passage of the material extracted, which was used in quantities as stated in the report. A two-holed cork admitted the entrance of steam and at intervals the other hole was used to allow the running in of boiling water, which served to wash out the soluble matter. The extracted liquor was collected in a liter flask until about 600 cc was extracted. The extraction was continued until the washings showed no color and this liquor, concentrated by boiling until the volume was about 300 cc (using a funnel in neck of flask to hinder admission of air), was added to that in the liter flask and after 12 hours made up to 1,000 cc.

C. W. Norris.—(The method used by Mr. Norris is substantially the same as that of Messrs. Alsop and Teas. *Referee.*)

F. P. Veitch.—One of the points which needs immediate attention, in my opinion, is the fineness of material and its effect upon extraction.

(Mr. Veitch's results were not received in time to be included in the comparative table, but owing to their interesting bearing on the subject the referee herewith appends them.)

TABLE XII.—*Results obtained by F. P. Veitch.*

[Total volume of liquor 5 liters, concentrated to 1 liter.]

Material.	Total solids.	Soluble solids.	Non-tannins.	Tannins.	Time of extraction.	Dry hide powder.	Amount of material.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Hours.*	*Grams.*	*Grams.*
Fresh bark	17.43	15.63	4.75	10.88	15	17.10	30
Spent bark	3.06	2.93	1.57	1.36	15	14.25	75
Chestnut wood	8.98	8.58	2.25	6.33	15	14.25	40

G. A. Kerr.—We use for extraction a percolation system, consisting of a copper cylinder 9 inches long and 2½ inches in diameter, reduced at the top by a cone-shaped shoulder and neck to 1½ inches and at the bottom to one-quarter inch, and fitted with a copper discharge tube of the same diameter. At the lower shoulder a false bottom of finely perforated copper is secured to act as a strainer.

The neck or top is fitted with a rubber stopper, through which is inserted the end of a block tin coil three-eighths of an inch in diameter and consisting in all of some 30 inches of tubing. The upper end of the coil is attached to a main pipe leading from a water still. In operation this pipe serves to conduct steam from the still, and the tin coil, acting as an air condenser, supplies an ample flow of water at steam heat to the cylinder, where it passes through the material to be extracted and is received in a flask placed directly under the discharge tube of the cylinder.

In order to avoid washing finely ground particles of the material through the strainer, it is our custom to cover it with a thin layer of cotton. This method was

devised by the writer to overcome the difficulty found in using the customary device, and having been found convenient, expeditious, and efficient, its use has been continued. It is understood that this device has also been adopted in other laboratories. There is no trouble in restricting the volume of liquor to 1 liter. A thorough extraction can be easily completed in 8 hours, and prolonged boiling is obviated. The progress of the extraction can at all times be seen and noted and test samples of liquor obtained without disconnecting the apparatus or interfering in any way with the process, and it is applicable to any tanning material. It is our custom to use 25 grams of new bark or wood. The quantity of spent material is governed by the average tannin content of the samples received at the laboratory, and these vary from 1.5 to 3.5 per cent tannin. In the case of absolutely unknown samples 50 grams dry are used. The quantity of hide powder is governed by the strength of the liquor obtained by extraction.

Study IV. Determination of Acids in Tan Liquors.

The referee herewith presents the report of the special committee on acid determinations, compiled by Mr. Teas, the other members of the committee being Mr. Eachus and Mr. Mosbaugh. The extent of the investigation and the painstaking care with which the work has been executed are strikingly shown by the report. The preponderance of opinion seems to be in favor of officially adopting the present provisional method, with the alternative of employing the cold method should it seem expedient to the analyst to do so.

The referee agrees that a more scientific method might be developed, but if this one yields comparative and concordant results, the necessity of sacrificing something to practicability, especially in laboratories where from 20 to 100 determinations must be made daily, is too apparent to need emphasis. Basing the value of this research upon the ability of the chemists who engaged in it, your referee would recommend that the method receive official recognition.

Report of the Subcommittee on Acid Determinations.

As an outline for the members of the subcommittee on acid determination to work upon, the following suggestions were made:

(1) That determinations of acid in liquors from bark, wood, etc., containing varying quantities of acetic acid, lactic acid, and mixtures of both acids be made, using charcoal with the solution hot and cold, and by shaking cold with the charcoal.

(2) That determinations by these methods be made on aqueous solutions of the same acids.

(3) That various quantities of charcoal and various strengths of tan liquor be used, as far as time permits, in order to make the range of the experiment as wide as possible.

The results of the experiments made on aqueous solutions undoubtedly show that some of the acid is neutralized by the charcoal. This could be taken care of by a factor depending on the quality of the charcoal, if the error was proportionately the same with different strengths of acid, and if this condition held true in the case of solutions containing tannin, which, in my opinion, it does not.

TABLE XIII.—*Acid determinations on distilled water mixtures containing known quantities of acid (Eachus).*

Method.	15 per cent solutions.		30 per cent solutions.		60 per cent solutions.	
	Acetic acid.	Acetic and lactic acids.	Acetic acid.	Acetic and lactic acids.	Acetic acid.	Acetic and lactic acids.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Hot	12	12	25	24	50	50
Cold	11	11	24	23	48	47
Shaker	11	10	24	23	47	47

In the above work 3 grams of charcoal were used, and boiling, stirring, or shaking continued 5 to 10 minutes. It will be noticed that the hot method gives results nearer the actual contents, i. e., higher than the cold methods, and this difference is manifest in all the experiments recorded in this report. Mr. Mosbaugh's figures on the clear acid solutions are slightly higher, which may be accounted for by the fact that he used 2 grams of charcoal. His results follow:

TABLE XIV.—*Acid determinations on clear acid solutions of known strength (Mosbaugh).*

[Two grams of charcoal used.]

ACETIC ACID SOLUTION.

Method.	Varying strengths of clear acid solutions.							
	0.8 per cent.	0.7 per cent.	0.6 per cent.	0.5 per cent.	0.4 per cent.	0.3 per cent.	0.2 per cent.	0.1 per cent.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Hot	0.7305	0.6405	0.5505	0.4485	0.3585	0.2655	0.1695	0.0825
Cold	.7230	.6315	.5370	.4395	.3540	.2565	.1605	.0765
Shaker	.7245	.6285	.5445	.4410	.3540	.2565	.1620	.0785

ACETIC AND LACTIC ACID SOLUTION.

Hot	0.7305	0.6345	0.5415	0.4455	0.3555	0.2625	0.1695	0.0825
Cold	.7215	.6285	.5340	.4395	.3495	.2550	.1605	.0765
Shaker	.7215	.6285	.5355	.4395	.3495	.2560	.1635	.0765

The influence of greater amounts of charcoal than the prescribed 2 grams is clearly shown in the following compilation:

TABLE XV.—*Influence of charcoal on acid determinations (Mosbaugh).*

ACETIC ACID SOLUTION.

Method.	Varying amounts of charcoal used.						
	2 grams.	2.25 grams.	2.50 grams.	2.75 grams.	3 grams.	3.25 grams.	3.50 grams.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Hot	0.3585	0.3540	0.3468	0.3393	0.3321	0.3276	0.3234
Cold	.3555	.3480	.3408	.3363	.3261	.3186	.3114
Shaker	.3555	.3480	.3468	.3363	.3291	.3246	.3174

TABLE XV.—*Influence of charcoal on acid determinations (Mosbaugh)*—Continued.

ACETIC AND LACTIC ACID SOLUTION.

Method.	Varying amounts of charcoal used.						
	2 grams.	2.25 grams.	2.50 grams.	2.75 grams.	3 grams.	3.25 grams.	3.50 grams.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Hot	0.3495	0.3450	0.3378	0.3303	0.3231	0.3186	0.3144
Cold	.3435	.3372	.3288	.3225	.3201	.3126	.3054
Shaker	.3435	.3390	.3318	.3246	.3213	.3156	.3084

The results on the determination of acids added to neutral tan liquors newly made are given in Table XVI. Mr. Eachus reports having used 12 cc of liquor diluted to 200 cc and 3 grams of charcoal, titrating with tenth normal sodium hydrate.

TABLE XVI.—*Acid determinations on neutral tan liquors of known acidity (Eachus).*

Method.	15 per cent solution.		30 per cent solution.		60 per cent solution.	
	Acetic.	Acetic and lactic.	Acetic.	Acetic and lactic.	Acetic.	Acetic and lactic.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
40° QUEBRACHO LIQUOR.						
Hot	13	14	29	29	58	59
Cold	12	13	27	27	56	59
Shaker	11	11	25	25	54	56
20° QUEBRACHO LIQUOR.						
Hot	14	14	28	28	59	59
Cold	12	13	26	27	58	57
Shaker	11	11	25	25	56	55
40° HEMLOCK LIQUOR.						
Hot	14	13	29	28	59	59
Cold	13	12	28	27	57	59
Shaker	11	11	27	25	56	57
20° HEMLOCK LIQUOR.						
Hot	13	13	28	29	59	59
Cold	13	12	28	28	58	57
Shaker	11	11	27	26	57	57
40° NEWLY MADE OAK LIQUOR.						
Hot	14	13	28	28	59	59
Cold	13	12	28	27	58	59
Shaker	12	11	26	25	56	57
20° NEWLY MADE OAK LIQUOR.						
Hot	14	14	28	28	58	59
Cold	13	12	28	27	57	58
Shaker	13	11	26	27	56	57

From the results obtained by Mr. Eachus, and from my own observation of the method, I am convinced that there is little loss of acid when a good charcoal is used in tan liquors containing a moderate quantity of tannin. Where there is a small amount of acid in a weak tan liquor the loss is greater. It is possible that the loss of actual acid is the same in strong liquors as in weak, and if this is so, there must be some compensating influence in the strong liquor which makes up for the loss. If, however, this compensating influence exists, it is not more marked in a 40° liquor than in a 20° liquor, which would seem to indicate that there is really no loss due to good charcoal when a moderate quantity of tannin is present.

Mr. Mosbaugh's results indicate the truth of the contention regarding the comparative effects of the presence of different amounts of tannin. He used a neutral hemlock liquor containing 0.92 per cent tannin, and his results are but slightly higher than results obtained from same amounts of acid used with distilled water. With 2 grams of charcoal he obtained the following:

TABLE XVII.—*Acid determinations on neutral hemlock liquor containing 0.92 per cent of tannin (Mosbaugh).*

[Two grams of charcoal.]

ACETIC ACID SOLUTION.

Method.	Varying percentages of acid.							
	0.8 per cent.	0.7 per cent.	0.6 per cent.	0.5 per cent.	0.4 per cent.	0.3 per cent.	0.2 per cent.	0.1 per cent.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Hot	0.7395	0.6435	0.5445	0.4485	0.3555	0.2595	0.1647	0.0687
Cold	.7215	.6285	.5337	.4395	.3465	.2505	.1575	.0645
Shaker	.7215	.6285	.5337	.4395	.3471	.2505	.1575	.0651
ACETIC AND LACTIC ACID SOLUTION.								
Hot	0.7380	0.6360	0.5445	0.4500	0.3570	0.2640	0.1680	0.0780
Cold	.7260	.6270	.5340	.4380	.3480	.2550	.1620	.0732
Shaker	.7260	.6270	.5340	.4380	.3480	.2550	.1605	.0732

On liquor solutions containing 0.4 per cent of actual acid, and using different amounts of charcoal, the results are shown in Table XVIII.

TABLE XVIII.—*Effect of using varying amounts of charcoal on acid determinations on a 0.4 per cent acid solution.*

ACETIC ACID SOLUTION.

Method.	Grams of charcoal used.						
	2	2.25	2.15	2.75	3.00	3.25	3.50
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Hot	0.3355	0.3510	0.3468	0.3411	0.3363	0.3309	0.3264
Cold	.3495	.3420	.3348	.3273	.3231	.3150	.3084
Shaker	.3495	.3435	.3366	.3303	.3261	.3186	.3114
ACETIC AND LACTIC ACID SOLUTION.							
Hot	0.3555	0.3480	0.3408	0.3333	0.3261	0.3219	0.3114
Cold	.3435	.3360	.3288	.3216	.3111	.3156	.3084
Shaker	.3435	.3390	.3318	.3243	.3201	.3192	.3084

While the discrepancy is greater in weak tan liquors and with small amounts of acid, yet the results are comparative. Since in any but weak solutions the results so nearly approach theory, and in view of the simplicity of the method, the facility of operation, and minimum chance of error, as compared with other methods, I favor for the present at least the continuance of the charcoal method. There are other methods probably more scientific, yet from the numerous operations involved the sources of error are multiplied, and in any but expert hands the results are accordingly unsatisfactory.

The results above show that there is nothing, with the possible exception of time, to be gained by the shaking method. Results from shaking are practically the same as from stirring the solutions. The hot-method results more nearly approach theory, but are not more concordant than the cold-method results, and require more time and attention, which is objectionable when a large number of acid determinations must be made.

In conclusion I wish to again recommend the charcoal methods, hot when possible, and cold when the number of analyses precludes the hot method. The charcoal used must be carefully watched and washed when necessary. The less charcoal used the better will be the results obtained on weak solutions. The dilutions may be the same as for nontannin work, and the time could be shortened if a weaker solution is used, provided the time for all acid determinations remains the same.

COLLABORATORS' NOTES ON STUDY IV.

C. Eachus, Yocum Manufacturing Company.—The work proves conclusively, in my opinion, that the charcoal method is satisfactory. Use 3 grams of charcoal and 12 cc of liquor made up to 200 cc with distilled water. Stir or boil from 5 to 10 minutes, filter and titrate 100 cc of filtrate with N/10 sodium hydrate. Each cubic centimeter of standard sodium hydrate equals 1 per cent acid. This is the method I followed, and had no trouble getting 40° liquors clear. Shaking has no advantage over stirring. Boiling and stirring give concordant results, and it appears that charcoal does not use up any acid when tannin is present in the acetic or lactic solution.

F. R. Mosbaugh.—In carrying out this work three methods were followed—hot, cold, and shaker. In the hot method the solution was heated to boiling in flask, using return condenser; the cold method, let stand in stoppered flask for 2 hours, shaking every 15 minutes, and in the shaker method gave 3 minutes' shaking in machine. S. and S. filter paper No. 590 and charcoal, rewashed in laboratory before using, were employed. In all cases 2 grams of charcoal (weighed within a milligram) were used. I checked all "chemically pure" acids against my standard solutions and used same flasks for all dilutions, which were made at 21.1° C, and this temperature was maintained throughout. The alkali used was N/10 sodium hydrate. Neutral hemlock liquor made from new bark, containing 0.92 per cent of tannin, was employed, and in all cases 100 cc of this was taken for determination, titrating 50 cc of filtrate.

The object of the first determination was to ascertain the effect of a given amount of charcoal upon liquors containing different amounts of acid, and with this in view eight solutions of acid, strength from 0.1 per cent to 0.8 per cent (as acetic) were made up. The second determinations were made to determine the effect of varying amounts of charcoal upon liquors of given acid value. For this solutions containing 0.4 per cent of acid as acetic were used, and from 2 to 3.5 grams of charcoal were used, varying 0.25 gram in each determination.

It is found to be necessary to detanninize as well as decolorize the liquor, and to accomplish this 1 gram of charcoal is necessary for 100 cc of liquor containing 0.1 gram of tannin, and when stronger the results are unsatisfactory.

All results are figured as acetic acid, and when a mixture of acetic and lactic acids were used equal parts (as acetic) were taken. Note that cold and shaker methods give results practically the same, but lower than the hot method—also that all methods produce results lower than theory, which does not support all of last year's association results in acid determinations. Also the error increases as the acid value of the liquor decreases, and where different amounts of charcoal are used the error is greater in proportion to the amount of charcoal used, all of which goes to show that it would be necessary to regulate the charcoal correction according to the amount of acid contained in liquor, and that the best that can be expected of the method are results to be used for comparison only.

Study V. Confirmation of Referee's Recommendations for 1903.

To confirm the recommendations as to the necessity of adopting specific means for the prevention of evaporation during filtration, a request was made for the determination of the solubles and insolubles in the official samples sent out this year—employing the means specified. Nine analysts responded, and upon tabulating their results it is found on comparison with the analyses of the same extract by the provisional method (Table I) that the soluble solids of chestnut extract are reduced on an average 0.22 per cent, those of the hemlock extract 0.32 per cent, and those of the quebracho 0.01 per cent, while the insolubles are increased to approximately the same extent.

The figures cited do not really give the true difference between results obtained without precaution against evaporation and those obtained under the recommendations, inasmuch as, since the referee suggested this source of error, more care has been taken to avoid variation from this cause.

Table XIX.—*Comparison of provisional method, and referee's modifications, 1903.*

Method.	Chestnut.		Hemlock.		Quebracho.	
	Soluble solids.	Insolubles.	Soluble solids.	Insolubles.	Soluble solids.	Insolubles.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Provisional	37.17	0.548	42.73	2.93	48.21	2.71
Referee's modifications, 1903	36.95	.87	42.41	3.26	48.20	2.57
Difference	.22	.322	.32	.33	.01	.14

Table XX.—*Analyses of various extracts by the provisional method, with referee's modification, 1903.*

HEMLOCK EXTRACT.

Analyst.	Total solids.	Soluble solids.	Insolubles.
	Per cent.	*Per cent.*	*Per cent.*
H. C. Reed	45.38	43.47	1.91
F. H. Small	45.64	40.90	4.74
H. T. Wilson	45.52	42.49	3.03
W. H. Teas	45.98	41.28	4.70
Harry Gerber	45.88	43.37	2.51
E. R. McCarthy	45.60	43.84	1.76
J. C. Scott	46.70	43.07	3.63
A. J. Stilwell	44.72	41.40	3.32
C. W. Norris	45.68	41.92	3.76
Average	45.68	42.41	3.26

TABLE XX.—*Analyses of various extracts by the provisional method, with referee's modification, 1903*—Continued.

CHESTNUT WOOD.

Analyst.	Total solids.	Soluble solids.	Insolubles.
	Per cent.	*Per cent.*	*Per cent.*
H. C. Reed	37.39	37.03	0.36
F. H. Small	37.63	36.77	.86
H. T. Wilson	37.51	36.69	.82
Harry Gerber	38.22	36.54	1.68
E. R. McCarthy	38.08	37.36	.72
J. C. Scott	38.51	37.53	.98
A. J. Stilwell	37.61	36.58	1.03
C. W. Norris	37.64	37.11	.53
Average	37.84	36.95	.87

QUEBRACHO EXTRACT.

H. C. Reed	50.29	47.65	2.64
F. H. Small	50.34	48.52	1.82
H. T. Wilson	50.41	47.83	2.58
W. H. Teas	51.07	47.10	3.97
Harry Gerber	50.66	48.72	1.94
J. C. Scott	51.45	48.42	3.03
C. W. Norris	51.02	48.34	2.68
E. R. McCarthy	50.99	49.04	1.95
Average	50.87	48.20	2.57

From numerous tests it has been found that a difference of at least 0.5 per cent soluble solids occurs, which would affect the tannin figure about 0.35 per cent. In any case it is fairly demonstrated that the precautions suggested assist in eliminating error, and your referee advises the adoption of the recommendations.

OBSERVATIONS OF COLLABORATORS.

Mr. Wilson.—Study V shows the necessity for guarding against evaporation during filtration. The tendency in these tests to reduce the soluble solids emphasizes the necessity of overcoming the filter paper absorption.

Mr. Eachus.—By filtering for soluble solids according to your recommendations we obtained 0.5 per cent lower soluble solids in the hemlock and quebracho samples, but no difference in the chestnut.

Mr. Scott.—My results indorse the referee's modification. The use of a ground stoppered weighing bottle is found convenient and necessary to accurate dilutions.

Mr. Stilwell.—I find difficulty in transferring rapidly and completely a highly concentrated liquor extract, such as the quebracho received, to a weighing bottle. With this exception I believe the weighing bottle is an improvement.

RECOMMENDATIONS.

It is recommended—

(1) That further research be made, with the object of establishing a limit of temperature at which the determination of soluble solids and insolubles shall be conducted.

(2) That the method for analysis of barks, woods, etc., as set forth in the foregoing report, be adopted as a provisional method, and trials continued until it has been perfected.

(3) That the present provisional method for the determination of acid in tannin solutions, with the alternative of using the cold charcoal method, receive official recognition.

(4) That the referee for 1905 make a study of present methods of analysis of tannery-yard liquors, especially spent or "sapped" liquors.

(5) That the recommendations submitted in the report for 1903 be embodied in the official (?) method.

The referee desires to thank the members of the tannin section generally, and the members of the research committees especially, for the active interest and assistance rendered during the past two years.

Following the report on tannin, Mr. Veitch presented in brief two papers, which are here given in full, and a discussion on the definition of tannin and the use of sucrate of lime in the Parker method for determining tannin, by Messrs. Veitch, Small, Reed, and Nichols, completed the consideration of this subject.

THE EXTRACTION OF TANNING MATERIALS WITH DIFFERENT EXTRACTORS.

By F. P. Veitch.

Owing to the fear that tannin may be oxidized by prolonged boiling, and to the fact that the extraction of certain materials gives maximum results only at low temperatures, a number of forms of apparatus have been used for the laboratory extraction of tanning materials. At present, however, but two extractors are in general use—the Koch or some modification of it, as that of Proctor, and a modified Soxhlet devised at the Vienna Research Laboratory and generally known as the Weiss extractor.

There are several objections to each of these extractors. With the Koch extractor the evaporation of the extract, which frequently amounts to from 2 to 4 liters, is a decidedly objectionable feature, requiring considerable time and encouraging to a certain extent the very thing it was designed to prevent, namely, the oxidation of the tannins by boiling. In addition, there is reason to believe that where the tanning material is put in the extractor dry, the most convenient way, there is often some channeling and the extraction is incomplete, as illustrated in the case of the spent hemlock bark given in the table. On the other hand, the Koch apparatus enables one to control the temperature of extraction as no other form does, and its use would seem to be advisable with materials high in starch.

Notwithstanding the fact that Eitner et al.[a] found that the Weiss extractor gave satisfactory results, tanning chemists have generally looked with misgiving on it, fearing oxidation during the long-continued boiling of the extract. Indeed, Hunt,[b] Proctor and Parker,[c] and Parker[d] have shown that for many materials less tannin is extracted at boiling than at lower temperatures. The total volume of extract in these experiments was only 1 liter, and it seems possible that longer extraction would have given higher results at the higher temperatures.

The International Association of Leather Trades Chemists has adopted the Koch extractor as official, and Proctor (Leather Industries Laboratory Book, and Principles of Leather Manufacture) regards the prolonged boiling of the extracted materials, such as takes place in the Weiss, as inadmissible.

On the other hand, in addition to Eitner et al., Boegh[e] has found that the Weiss extractor gave higher results than the Koch extractor on oak and pine bark, valonia,

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[a] Der Gerber, 1887, p. 3.

[b] J. Soc. Chem. Ind., 1885, *4:* 263.

[c] Ibid., 1895, *14:* 635.

[d] Ibid., 1898, *17:* 106.

[e] Abstract J. Soc. Chem. Ind., 1899, *18:* 303.

sumac, and quebracho wood, and gave lower results on divi-divi and myrobalans. The Weiss extractor is also used in most tannery laboratories in this country in extracting woods and barks, with satisfactory results.

It thus seems that there is considerable difference of opinion as to the accuracy of the results and the losses of tannin obtained with these two methods of extraction. I have therefore endeavored to avoid the difficulties and objections presented by these generally used methods by substituting an extractor with which the evaporation and concentration of large volumes of dilute liquors necessary by the Koch method is avoided, and with which the prolonged boiling of the gradually strengthening extract and its frequent concentration and dilution, as with the Weiss method, is not necessary.

Such an extractor is found in the old and well-known inner tube, continuous extractor, or in the side tube extractor devised by Zulkowsky. With the former the extraction takes place at 100° C, with the latter at 90°–95°. Undue concentration and boiling of the extract is avoided by placing only about 250 cc of water in the receiving flask, and after the extraction has continued a short time replacing the receiving flask by another containing the same amount of water. This is repeated at longer intervals, until the extraction is completed, the total volume of extract being kept within a liter. If it is desired to extract the first portions at lower temperatures, the heated water may simply be poured on the material in the extractor until 500 cc have passed through, and the extraction may then be finished at steam heat.

Comparative results which have been obtained with all three forms of extractor are given in the table. The extraction was continued for 2 working days, or about 15 hours, with the Koch extractor being the same for all samples. It was found desirable to thoroughly wet the material before putting it in the continuous extractor thus overcoming any tendency to channeling. A perforated porcelain plate placed on top of the firmly pressed material distributes the condensed water, and, being prevented from rising far by coming in contact with the end of the condensing tube, prevents loss of material which is apt to be caused by the occlusion and expansion of the air and steam in a finely ground sample.

The results marked (1) were obtained with the Weiss, (2) with the Koch, and (3) with the continuous extractor. The samples include all our generally used native tanning materials except chestnut-oak bark.

In examining the results, total solids may be omitted from consideration, as this determination often includes some of the material which was carried over into the extract. This is particularly true of the results with the Weiss extractor. Although the solid material was given time to settle before drawing out for total solids, not much importance is attached to these results.

Soluble solids were highest by the continuous extraction, except in the case of chestnut wood, where, I believe, the coarseness of the sample was in favor of the Weiss extractor. The Weiss extractor gives higher results than the Koch extractor, except on one sample of tan oak bark. Tannin is highest with the continuous extractor, except with sumac, where, notwithstanding the lowest soluble solids, tannin is the highest when the Koch extractor was used. No conclusion, however, can be drawn from one sample.

As a rule, it appears that where the extraction is continued for some time, all constituents, reds, nontannin, and tannin, are removed in somewhat larger quantities by using the continuous extractor. Except in the case of sumac, there is nothing to indicate that there is any serious loss of tannin, or rather any material difference in the loss of tannin from any cause, with any of the extractors. While reds and nontannin are usually higher when the continuous extractor is used, this fact, in the presence of high tannin, is not conclusive evidence that any loss of tannin has

occurred. As has been said, apparently larger amounts of all soluble constituents have been dissolved.

The conflicting results obtained by different investigators on the effect of heat on the extraction of tannin and on its oxidation renders further investigation very desirable. Partial explanation of these conflicting results may be found, perhaps, in the small quantity of water used for extraction in the Koch extractor, and also in the custom of beginning the extraction at a low temperature, and finishing at 100°. Proctor and Parker in their investigation of the effect of temperature, extraction with only 1 liter of water, and text-books generally, lead one to understand that complete extraction may be secured with 2 liters or less of water. My experience leads me to doubt this very much, as I usually find tannin being removed in considerable quantities, after extracting with 3 or 4 liters for 8 to 12 hours. Further than this, if all the tannin is not extracted at low temperatures, and it is true that high temperatures cause the starches to hold back tannin, it appears reasonable to think that this will occur with the last portions of the tannin as well as the first—and possibly to a greater degree, if the tannins extracted at a higher temperature are more insoluble than those extracted at low temperatures.

I am inclined to think, from a consideration of the results obtained, that, in the early stages of extraction at boiling temperatures, the tannin is partly precipitated or held back by the gelatinized starch, but that it is entirely dissolved and removed if the extraction be continued long enough. This, I believe, requires about 16 hours. Further investigations with other materials will be made in the leather and paper laboratory of the Bureau of Chemistry.

TABLE I.—*Comparison of results obtained with three different extractors.*

[1, Soxhlet; 2, Koch; 3, continuous.]

Sample No.	Material.	Extractor.	Total solids.	Soluble solids.	Reds.	Nontannin.	Tannin.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per ct.*
2556	Bark of tan bark oak calf.	1	27.04	26.06	0.98	.....	.....	1.66
		2	27.38	26.82	.56	10.60	16.22	.....
		3	29.66	28.68	.98	.....	.....	1.44
2532	Bark of tan bark oak calf—"Rump bark."	1	45.76	43.72	2.04	.....	.....	.60
		2	44.92	42.06	1.86	12.86	29.20	.....
		3	47.64	45.48	2.16	.....	.....	.52
2592	Pecan shells	1	12.72	12.08	.64	.....	.....	.....
		2	11.36	.....	.....	1.73	9.63	.....
		3	13.24	12.52	.72	.....	.....	.....
.....	Hemlock bark, new	1	18.47	16.10	2.17	.....	.....	.....
		2	17.43	15.63	1.80	4.75	10.88	.....
		3	23.10	19.37	3.73	7.48	11.89	.....
.....	Hemlock bark, spent	1	.....	.....	.....	.....	.....	.....
		2	3.06	2.93	.13	1.57	1.36	.....
		3	8.29	7.24	1.05	.....	.....	.....
.....	Chestnut wood	1	13.68	12.28	1.40	4.75	7.43	.....
		2	8.98	8.58	.40	2.25	6.33	.....
		3	12.50	11.20	1.30	3.63	7.57	.....
.....	Sumac leaves—coarse ground.	1	52.05	49.70	2.35	28.54	21.16	.....
		2	47.42	45.72	1.70	20.74	24.98	.....
		3	53.57	49.85	3.72	27.29	22.56	.....
.....	Sumac leaves—fine ground	3	53.12	49.70	3.42	25.92	23.78	.....

A DISCUSSION OF METHODS FOR THE ESTIMATION OF TANNIN.

By F. P. Veitch.

The method known as the hide-powder method, while not formally adopted as official by this association, is used exclusively for the estimation of tannin in tanning materials. It is well recognized, however, that the method yields inaccurate results. The chief sources of error appear to be a continuous absorption of solids from the solution by the filter paper during the preceding determination of soluble solids, and an undoubtedly greater error due to the absorption of coloring matter and other nontannin matters by the hide powder. The first may produce a minus error, the latter produces a plus error. Experimental demonstration is hardly needed of the fact that hide powder removes other constituents than tannin from tannin solutions brought in contact with it, as such absorption, occlusion, etc., is a common property of all precipitates or other solid matter in contact with solutions of solids, and prolonged washing is frequently required to free them from materials held in this way. Nevertheless we have experiments showing that in addition to tannin most of the nontannin constituents common to solutions of tanning materials are absorbed to a serious extent by hide powder, as may be seen from the work of Proctor and Blocksey,[a] who found the absorption of gallic acid, quinol, catechol, and catechin when present in solution with gallo-tannic acid or quebracho tannin was from 44 per cent to 106 per cent of the amount present. Dextrin and glucose were absorbed in very much smaller quantities or lowered the absorption of the tannin.

A lively appreciation of these facts, together with the time and work required to obtain results, has greatly stimulated the search for more accurate and quicker methods. The methods and proposals which have appeared as a result of this activity are of such a character that, while I can not offer anything better than the hide-powder method, a few words of criticism and a brief statement of what must be avoided would seem to be timely, and may be of service to many who at first sight are favorably impressed with some of these methods.

Most of the effort has been directed along the lines of the precipitation of tannin by metallic oxids, or along the lines suggested by the Löwenthal method. The effort to determine tannin by precipitation with metallic oxids dates back almost to the infancy of analytical chemistry, and the idea has been tried and abandoned under all kinds of conditions a number of times. There is no doubt that tannin in pure solutions can be determined with metallic oxids, but so far no one has proposed a method which will quantitatively separate tannin from closely related nontannins and coloring matter such as are always present in solutions of tanning material.

A moment's consideration of the chemical processes involved in dyeing and in the preparation of lake colors is sufficient to convince one that the separation of tannin from the above-mentioned nontannins is not a simple operation. As a matter of fact, the methods used in mordant dyeing and in the preparation of lakes are the same in principle as those which have been proposed for the separation and estimation of tannin. To make matters worse, tannin is one of the substances which may be used with basic coloring matters to insure a precipitation with metallic oxids, which would not otherwise take place. Such basic colors are not usually present in tanning materials, however. From these facts it is obvious that before we can hope to quantitatively separate tannin from the colored and colorless nontannins with which it is usually associated, by the use of metallic oxids, we must develop some means of preventing the coprecipitation or occlusion of these nontannins or remove them from the tannin precipitate by the use of a wash solution which does not attack the tannin.

Just here it may be said that as the more or less complete removal of coloring matter

[a] J. Soc. Chem. Ind., 1903, *22:* 482.

is common to hide powder, gelatin, and metallic oxids, the tanning value and weight-giving qualities, or, in other words, the leather-making qualities, of these coloring matters must be established as a foundation upon which to build any reliable method.

Two methods based on the use of metallic oxids have been proposed during the past two years. Rous[a] proposes to precipitate tannin with a ferric salt in the presence of a tartrate and acetic acid. The method consists in adding to 50 cc of tannin solution (containing about 0.4 gram of tannin per 100 cc), 10 cc of one-half normal carbonate of soda, 10 cc of one-half normal ferric sulphate or ferric alum, and 25 cc of 6 per cent acetic acid containing 5 grams of neutral sodium tartrate per liter. The whole is stirred vigorously, boiled one minute, filtered, washed free of iron with hot water, ignited, and weighed. The weight of the ferric oxid multiplied by 4.024 equals tannin. The reagents must be so adjusted to each other that when 10 cc of sodium carbonate and 10 cc of the ferric salt are mixed, boiled, and filtered, the filtrate must be faintly acid to methyl orange. After boiling five minutes a mixture of the reagents in the proportions used in the determination must remain clear and bright.

The author claimed that the washed precipitate of iron and tannin is of constant composition and assigned to it the following formula—$(C_{14}H_7O_9)Fe$. Washing the precipitate with dilute acetic acid or normal acetic acid dissolved out iron but not tannin. Accurate separation from gallic acid was claimed, but no separation from other closely related compounds was attempted. It was stated that when different quantities of tannin were contained in the same volume of solution the resulting precipitate varied proportionately.

My own work with this method has led to the following conclusions:

With any given tannin solution, maintaining strictly identical conditions as to volume and strength of reagents, duplicates on total weight of precipitate and on the iron it contains are obtained.

Changing the strength of acid in which the precipitation is made changes the amount of iron in the precipitate.

The weight of the precipitate and its iron content do not vary proportionally with the concentration of the tannin solution; that is, when the weight of tannin in the given volume of solution is doubled the weight of the precipitate and of the iron in it is not equally increased.

With different tanning materials the proportion of iron in the precipitate varies greatly, so that it is utterly impossible to establish any relation between the tannin precipitate and the amount of iron it contains.

The nature of the relation between the tannin and the iron in the precipitate the writer has not been able to establish. In this we have another close analogy to the lakes, where this relation has never been definitely established.

Precipitation of tannin appears to be complete; at least no precipitate is obtained by adding a few drops of 1 per cent gelatin solution to the filtrate. A larger quantity of gelatin gives a bulky white precipitate, which is also given by the reagents alone, without tannin. Pyrogallol has been found to precipitate iron in the same way that tannin does, and so has the nontannin filtrate from sumac. Water-white, nontannin filtrates from barks, quebracho, and chestnut extracts do not give a precipitate.

Thus in its present form the method is inapplicable to tanning material, but the indication that the iron content of the precipitate may be varied almost at will, without changing materially the organic precipitate, is suggestive, and it may be possible to remove it entirely, leaving tannin or a decomposition product from which tannin may be calculated. I hope to investigate this point further, for even if the method should not be applicable to the estimation of tannins, some light may be thrown on their nature and constitution.

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[a] Zts. anal. Chem., *41*: 717.

Wislicenus[a] proposes to estimate tannin by absorbing it with an aluminum hydroxid or oxid made by acting on aluminum with 5 per cent caustic soda and a trace of mercuric chlorid. The absorption of the tannin is hastened by mechanical agitation. Gallic acid is also almost completely absorbed, but can be removed by washing. The results obtained when the aluminum tannate was washed agreed fairly well with results obtained by the hide-powder method on a pure tannin, oakwood extract, oak bark, and chestnut extract. The unwashed precipitate weighed too much. This agreement with the hide-powder method is enough to condemn the method so far as accuracy is concerned. If this agreement with the hide-powder method be confirmed on all materials the method may have some claim to consideration, as aluminum hydroxid can be prepared in large quantities and kept indefinitely, thus doing away with one very objectionable feature of the hide-powder method.

Parker and Payne[b] propose to estimate tannin by determining the amount of calcium hydrate neutralized before and after removing the tannin with a specially prepared gelatin solution. This method is a return to the principles of the old Löwenthal method, which has been abandoned chiefly because different tanning materials can not be compared with each other by its use. We do not know that the reducing power of the catechol and pyrogallol tannin is the same, or even that the several tannins of these two groups have the same reducing power for permanganate, or acidity with respect to calcium hydrate. The method consists of adding 300 cc of N/5 calcium hydroxid to 200 cc of a clear tannin liquor of the official strength; let stand 7 hours in a stoppered flask, shaking frequently, filter and titrate 100 cc of the filtrate, using phenolphthalein as indicator, and calculate the quantity of calcium hydrate absorbed by the 200 cc of tannin solution. This gives the total absorption value of the liquor.

Two hundred cc of the original tannin solution are then mixed with 100 cc of N/5 acetic acid and 100 cc of Collin solution, which is prepared by dissolving 60 grams of good gelatin in 500 cc of water, warming until dissolved, and treating with 120 cc of normal caustic soda, heating on the water bath at 90° for 20 minutes, filtering through linen, neutralizing to phenolphthalein 500 cc of the filtrate with normal acetic acid, and making the whole up to 1 liter, adding 1 cc of chloroform to preserve it. In the presence of acetic acid the Collin solution completely precipitates the tannin, which is filtered off, 200 cc of the clear bright filtrate placed in a flask, and 200 cc of N/5 calcium hydrate added. This is well shaken, allowed to stand for 1 hour, and the absorption of calcium hydroxid determined. After correcting for the acetic acid, we have the absorption minus tannin, which, subtracted from the total absorption, gives the absorption due to tannin, from which the percentage of tannin is calculated. The authors have found that 1 gram of carefully prepared and pure gallotannic acid absorbs exactly 125 cc of N/5 calcium hydroxid, which corresponds to the following reaction:

$$C_{14}H_{10}O_9 + Ca(OH)_2 = C_{14}H_{10}O_9Ca_4(OH)_8.$$

It is not stated that other tannins have the same value except that 1 gram of ellagic acid is said to absorb 125.9 cc of N/5 calcium hydroxid. From the total absorption figures results agreeing well with the results by the hide powder method are obtained, while the corrected figures give much lower results.

The authors found that the Collin precipitate of amorphous leather is easily removed from the linen or from the filter paper upon which it is, and if well washed in water, dried, weighed, and the nitrogen determined, the weight-giving capacity of the material is found.

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[a] Zts. angew. Chem., 1904, *25:* 801.

[b] J. Soc. Chem. Ind., *23:* 648.

The accuracy of this method will depend largely on two things; first, whether all tannins have the same absorption value for calcium hydroxid as gallotannic acid has, and, second, whether the precipitation of tannin by gelatin or the Collin solution is complete under the conditions of the method. On these points I think one may be pardoned for being somewhat skeptical. There are a number of unexpected statements in this paper. For instance, we note that "pure tannic acid does not precipitate 'Collin' (gelatin) without the addition of a tanning adjunct, i. e., organic acid," and that "the majority of tanning materials depend upon the anhydrous digallic acid content for their activity as tanning agents." "N/5 calcium hydroxid" would be considered a typographical error did it not occur so frequently, and as it is difficult to obtain even an N/20 calcium hydroxid solution, it is important to know just what is meant, for, with different strengths of alkali, tanning materials have a different absorption factor, and no check of the proposed method can be made by others until some explanation of the phrase is given. [a]

Perhaps the most interesting statement in the whole paper is that the tannin Collin precipitate can be washed with water, dried at 100°, weighed, and Kjeldahled, thus giving the weight-producing capacity of a tanning material and actually checking the method. If this statement is confirmed it would seem that all difficulties would be solved, but such a thing has never been satisfactorily accomplished before.

For more than a year I have been working at odd moments along lines similar, but not identical, to those of the Parker method, but without definite results—indeed, with rather unfavorable results. An attempt to duplicate the work of Parker and Payne came to nothing on account of inability to obtain a N/5 calcium hydroxid solution. A barium hydroxid solution did not give results near theory on a practically pure gallotannic acid. Admitting the accuracy of the results obtained on pure gallotannic acid by this method, I believe that we must wait for the proof that other tannins have the same reaction with limewater before the method can be regarded as having a practical value.

Although I have made numerous experiments with a good commercial (medicinal) gallotannic acid with chestnut, quebracho, and oak extracts, I have never been able to completely precipitate the tannin with gelatin, using the Parker and Payne method—the filtrate always contains both tannin and gelatin. This, however, may be my fault, and greater familiarity with the method or a correction of the evident error regarding the strength of the limewater, and consequently of the acetic acid, may lead to better results.

In conclusion, while no method is known which promises better results than the present method, we should not rest satisfied with it, but endeavor to devise a substitute which shall have a firmer foundation both in theory and in its relation to tannery practice. With this object in view efforts have been made for some time in the Bureau of Chemistry to obtain a complete precipitation of tannin with gelatin in such form and purity that it may be dried, weighed, and its composition determined. So far they have been unsuccessful, but the investigation has not been abandoned.

At the close of the discussion on tannin, Mr. Carpenter, referee on potash, asked permission to present a paper bearing on that subject on behalf of Mr. Donk. The following article was presented.

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[a] It has been learned since this paper was written that a N/5 solution of sucrate of lime was meant.

EXPERIMENTS ON THE VOLUMETRIC ESTIMATION OF POTASH AS PHOSPHOMOLYBDATE.

By M. G. Donk.

At the meeting of this association in 1902 the writer called attention, in connection with the potash work for that year, to the precipitation of potash as phosphomolybdate affording a possible means of recovering all the potash in mixtures containing acid phosphate. The reaction involved is a parallel to the precipitation of phosphoric acid with ammonium molybdate potash replacing ammonia in the precipitate. The precipitate formed when ammonium molybdate is added to a solution containing a phosphate is, as is well known, the ammonia salt of phosphomolybdic acid and the feeble solubility in water of its potash salt is the basis of the process on which this work has been done. Just as a phosphate is precipitated by addition of ammonium molybdate or ammonia by adding a soluble phosphomolybdate or free phosphomolybdic acid, so potash may be removed from solution as potassium phosphomolybdate in presence of lime, magnesia, iron, phosphates, etc., since only ammonia, potash, and thallium salts form insoluble compounds with phosphomolybdic acid.

The term precipitate used in connection with this potash compound is not literally correct. The so-called precipitate is the residue obtained by evaporating the potash solution, to which the precipitant has been added, to dryness, when the yellow potassium phosphomolybdate crystallizes out and remains as an insoluble residue when exhausted with acidulated water to remove excess of reagent, lime, etc. It is a peculiarity of this body that although very insoluble in water (1 part in 14,000), and correspondingly difficult to dissolve, it can only be precipitated from very concentrated solutions and even then not completely, though when evaporated with the reagent combination readily takes place.

Raulin,[a] it appears, was the first to work out a method based on the insolubility in water of potassium phosphomolybdate published in 1890, and in 1898 Wavelet had published an account of his work on "The determination of potash by means of phosphomolybdic acid."[b]

The following is Raulin's method in brief: A reagent is prepared by adding aqua regia (hydrochloric and nitric acid 1–1) to a solution containing 100 grams of ammonium molybdate and 6.5 grams ammonium phosphate in 250 cc till the precipitate formed is redissolved. Evaporated to dryness, with frequent additions of small portions of hydrochloric acid, 400 cc of water, containing 5 cc hydrochloric acid, is added, warmed, allowed to settle, and decanted, when the solution is ready for use. A wash solution is prepared by adding to 1 liter of sodium nitrate solution, containing 20 grams per liter, 20 cc of phosphomolybdic acid, 2 cc of nitric acid, and 2 cc of a niter solution containing 80 grams per liter. The mixture is warmed, shaken to saturate it with potassium phosphomolybdate, allowed to settle, and filtered. To a portion of the potash solution containing presumably 15 milligrams of potash converted to nitrate and evaporated to small bulk, about 10 cc of the reagent are added, evaporated to dryness at 50°, transferred to a small double filter (balance), and washed with 60 cc of the wash solution. The blank filter is also saturated with the wash solution and the two dried at 50° to constant weight. The corrected weight multiplied by 0.052 gives the potash as K_2O.

Wavelet determines phosphoric acid in the potassium phosphomolybdate, which, multiplied by 1.99, gives the potash. He prepares a reagent by dissolving 70 grams of freshly ignited molybdic acid in 500 cc of a solution containing 140 grams of

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[a] Compt. rend., *110:* 289; reprinted in Ann. chim. anal., 1900, *5:* 345.

[b] Bul. Soc. chim. du nord de la France, 1898; Ann. chim. anal., 1900, *5:* 289; abstract, Chem. Centrbl., 1900, *2:* 689; Exper. Stat. Rec., *12:* 713.

sodium carbonate and 20 grams of sodium phosphate. Two hundred cc of nitric acid is added, the solution made up to a liter, allowed to stand 24 hours, and filtered. For the determination 10 grams of material are dissolved in 200 cc of water, to 20 cc of which an excess of reagent is added and evaporated to dryness on the water bath. To the powdered residue 40 cc of 10 per cent nitric acid is added, warmed on the water bath, and allowed to stand till cool, when the precipitate is transferred to a filter and washed with 10 per cent nitric acid, after which it is dissolved in a minimum of ammonia, and the phosphoric acid precipitated with magnesia mixture, as usual. The weight of phosphoric acid found multiplied by 1.99 gives the potash.

No figures are given in Raulin's account of his method to show its accuracy as compared with results obtained by a known method, but experience with the drying and weighing of potassium phosphomolybdate precipitates shows that the method must of necessity be tedious and unreliable, for it is difficult to retain the precipitate on the best S. and S. filter, filtration is exceedingly slow, due to clogging, and the dry precipitate is very hygroscopic, while the use of balanced filters impregnated with salts of the wash solution must be a fruitful source of error and the use of a gooch is impracticable. I have tried Wavelet's method on a number of fertilizer samples analyzed in the laboratory by the official method, and although the author claims it to be reliable from results obtained with salts and solutions of known composition (for which, however, no figures are shown in the article mentioned), my results were all low and very irregular. These variations I traced to the difficulty of washing out the excess of reagent used without also dissolving or washing through the filter a portion of the precipitate; while the general low results were found to be due to the great solubility of the precipitate in the strength of acid used in exhausting the evaporated residue and subsequent washing.

A solubility test of the precipitate in 10 per cent nitric acid at room temperature (about 30°), showed 1 part of the precipitate to be soluble in 491 parts acid. The possibility of titrating the yellow precipitate and thus making it a direct volumetric method of estimating potash, generally applicable, is what has interested me from the beginning. To accomplish this it was necessary to find a neutral liquid that could be used in obtaining the precipitate free from excess of reagent used and the nitric acid in presence of which it is formed. Water does not answer, in that it decomposes the precipitate with separation of molybdic acid. After trying and comparing a long list of substances the one found to be most suitable was a 0.5 per cent solution of sodium nitrate saturated with potassium phosphomolybdate, shaken at intervals for several days with about a gram of the yellow precipitate well washed with sodium nitrate solution of the same strength and filtered. The filtration is best performed with a carbon filter having a perforated plate in the bottom, covered with a layer of soft fibrous asbestos about an eighth of an inch thick, carefully packed down with a glass rod. When a good quality of asbestos is used and the mat thus prepared it is possible to filter and wash the yellow precipitate in a few moments without loss or difficulty of any kind.

The success of precipitating potash as phosphomolybdate depends in a large measure on the purity of the reagent used in precipitating. For a long time concordant results could not be obtained, being invariably higher with a solution prepared from sodium carbonate or hydrate than when a solution prepared by dissolving ammonium phosphomolybdate in aqua regia was used. This was found to be due to the separation from the former solution of molybdic acid not redissolved when the evaporated residue is exhausted with acidulated water. The best results are obtained with a solution of pure phosphomolybdic acid containing 100 grams per liter and acidified with 250 cc of nitric acid (sp. gr. 1.42). This reagent with potash salts of nitric, hydrochloric, and sulphuric acid on evaporation gives a beautiful precipitate of tabular crystals easy to handle on the filter and readily washed by decantation.

With the means for obtaining a pure precipitate at hand, the ratio of potassium

oxid in potassium phosphomolybdate to the alkali required to dissolve it was determined. To do this the precipitate from 0.1 gram of potassium nitrate was titrated with N/10 sodium hydrate (free from potash) and the potash determined in the solution thus obtained by filtering from the suspended asbestos, precipitating phosphoric and molybdic acid with lead acetate, evaporating the washings and filtrate to small bulk with addition of a slight excess of sulphuric acid to precipitate excess of lead acetate added, transferring to a platinum dish and igniting the evaporated residue (covered with acid-digested sand to prevent loss from spattering), and completing the potash determination as usual. From two such determinations 1 cc of N/10 alkali was found to be equivalent to 0.575 milligrams of potassium oxid in the yellow precipitate; that is, a sodium-hydrate solution for titrating potassium phosphomolybdate, 1 cc of which shall be equivalent to 1 milligram of potash, should be of such strength that 1 cc of this alkali is equivalent to 1.739 cc of N/10 acid. Having prepared a solution of that strength, it was used in titrating the precipitates from a number of potash samples with the results shown below, using phenolphthalein as indicator.

Determination of potash in different materials by official and volumetric methods.

Method.	C. P. nitrate of potash.	Commercial muriate of potash.	H. G. sulphate of potash.	H. G. tobacco dust.	Mixed fertilizer.	
					No. 1.	No. 2.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Official	46.55	50.56	50.50	9.72	3.17 13.20	10.41 10.50
Volumetric	46.21	50.02	50.08	9.65	13.49	10.43

These determinations are the first made by the writer by this method and have only just been obtained. For the potash salt 2.5 grams of material was dissolved in water and diluted to 500 cc, 25 cc of which, corresponding to 0.1 gram of material, was taken for analysis. Twenty cubic centimeters of the phosphomolybdic acid solution, prepared as described, were added and the mixture evaporated to dryness on the water bath in a casserole. The residue is exhausted with 25 cc of 0.5 per cent nitric acid, warmed to 50°, allowed to cool and washed with the sodium nitrate solution (prepared as described) three times by decantation, and finally on the asbestos filter, using not to exceed 150 cc of wash solution.

The sample of tobacco dust, of which 5 grams were taken for analysis, was treated with sulphuric acid and incinerated in the usual way for such material. Of the two samples of mixed fertilizer, which were composed of sulphate of ammonia, sulphate of potash, and acid phosphate, 5 grams were taken for analysis, ignited with addition of 2 cc of 1–1 sulphuric acid and water to drive off ammonia salts and destroy organic matter. The residue was then dissolved in water with the aid of 10 cc of hydrochloric acid, filtered after diluting to 500 cc, 25 cc taken for analysis and treated like the solution of potash salts without further manipulation.

The results are very gratifying, though it is recognized that the data are insufficient for the drawing of final conclusions and that much work is still necessary to establish the reliability of this method. Especially must the strength of the alkali solution, 1 cc of which is taken to represent 1 milligram of potash, be further verified. The method is exceedingly rapid and easy of execution, necessitating no operation by which loss of potash is liable to occur. The strong feature of the method is that it is possible thereby to determine potash in the presence of those substances the necessary removal of which occasions loss in the official method. This consideration, together with the few operations necessary, will, it is believed, make this

method a valuable supplement to the one now used by the association. I am confident that the results herein submitted can be duplicated by anyone following the directions given and do not hesitate to commend the method to the association. The method will be further studied, comparing the results obtained with those given by the official method, and it is hoped that the association will investigate its merits and by the cooperation of its members place the method on a working basis.

The referee on foods and feeding stuffs reported that owing to press of other matters no cooperative work on the subject had been done and that there was no report to be made.

The reports of special committees not being ready the presiding officer called for the report of Committee A on the recommendations of referees, which was given by Mr. Williams:

REPORT OF COMMITTEE A ON RECOMMENDATIONS.

C. B. Williams, *Chairman.*

(Phosphoric acid, potash, nitrogen, soils, ash and insecticides.)

1. Soils.

It is recommended—

1. That the investigation of methods for the determination of water-soluble plant food in soils be continued. [Adopted.]

2. That methods for determining the easily soluble plant food be further investigated by using acid solutions of greater strength than N/200, as was recommended by the referee last year and briefly reported on by Professor Peter in the referee's report. [Adopted.]

3. That this association encourage the reporting of soil analyses, as far as practicable, upon the uniform basis of chemical elements.

[A discussion on this recommendation brought out the fact that while uniformity in reporting all analytical results was greatly to be desired it was not deemed advisable, and would bring no relief to adopt such a measure unless it were concurred in by others, Mr. Wheeler emphasizing the point that the comparison of results obtained by the association with those reported by other chemists, especially Europeans, must be considered. The discussion resulted in the adoption of the following resolution made by Mr. Davidson:

Resolved, That a committee of five be appointed to consider the whole question of unifying the terms in which analytical results are reported, and report to the association at its next meeting.]

2. Ash.

It is recommended—

1. That the study of the nitric acid and peroxid methods be continued next year. [Adopted.]

2. That the referee on ash for the next year be requested to make determinations of the total sulphur in the samples used for cooperative work by the Barlow-Tollens or "absolute" method for sulphur in organic combinations. [Adopted.]

3. Nitrogen.

It is recommended—

1. That the alkaline permanganate method, amended to read as stated below, be adopted as a provisional method.

ALKALINE PERMANGANATE METHOD.

Weigh out an amount of sample containing 0.045 gram of organic nitrogen, and transfer to a 600 cc distillation flask. After connecting with the condenser to which the receiver containing standard acid has been attached, digest with 100 cc of alkaline permanganate solution (16 grams of $KMnO_4$ and 150 grams of sodium hydrate, dissolved in water and made to bulk of 1 liter) for 30 minutes below the boiling point. Then boil until 85 cc of distillate is obtained. If the material shows a tendency to adhere to the sides of the flask an occasional gentle rotation is necessary during distillation.

[After some discussion as to whether 100 cc of the alkaline permanganate solution were sufficient the recommendation was adopted.]

2. That the study of availability by both neutral and alkaline methods be continued, particularly with a view to determining the amount of material to be used in the neutral method on commercial fertilizers. [Adopted.]

4. Insecticides.

It is recommended—

1. That methods I and IV of the four modifications of the Avery-Beans method of determining total arsenic in Paris green be adopted as optional official methods.

[It being the first year that the adoption of these methods as official had been recommended, they were referred to the association for final action in 1905, in accordance with the established precedent in changing or making additions to official methods.]

2. That in titration of arsenic, N/20 instead of N/10 iodin be used, as Mr. Davidson suggests. [Adopted.]

3. That the electrolytic method be adopted as the official method of determining copper in Paris green and copper carbonate, and that the thiosulphate method be adopted as an optional method, using N/20 instead of N/10 thiosulphate solution.

[Finally adopted through the words "copper carbonate," having been brought before the association in 1903, and the remainder of the recommendation referred to the association for final action in 1905.]

4. That the work on London purple be continued. [Adopted.]

5. That the volumetric silver nitrate method be adopted as the official method of determining cyanogen in potassium cyanid, and that a N/20 instead of a N/10 solution of silver nitrate be used.

[Finally adopted, having been before the association in 1903.]

6. That the methods of examination of soda lye be further tested. [Adopted.]

7. That the Kissling method of determining nicotin be adopted as the official method, and that Mr. Emery's polariscopic method be further tested.

[Finally adopted, having been before the association in 1903.]

8. That the hydrogen peroxid method, suggested by Mr. Avery, for determining sulphur in sulphur dips and similar compounds, be adopted as a provisional method and tested by the association next year. [Adopted.]

9. That the Blank and Finkenbiener peroxid method be adopted as the official method of determining formaldehyde in strong solutions, and that the Romijn potassium cyanid method be adopted as an official method for analyzing dilute solutions.

[Recommended for the first time and action accordingly deferred until the meeting of 1905.]

10. That methods of comparing chlorid of lime be compared. [Adopted.]

11. That attention be given to the analysis of crude oil in disinfectants. [Adopted.]

5. Potash.

It is recommended—

1. That the directions for making the solution in mixed fertilizers given under the determination of potash in Bulletin 46, page 21, be made to read as follows:

Boil 10 grams of the sample with 300 cc of water plus 5 cc of hydrochloric acid for 30 minutes. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Add sufficient powdered ammonium oxalate to precipitate all the lime present, cool, dilute to 500 cc, mix and pass through dry filter.

The method for the solution of potash salts remains as it is.

2. That the directions for the determination of moisture in potash salts, sodium nitrate, and sulphate of ammonia, given under the determination of moisture, Bulletin 46, page 11, be made to read as follows:

In potash salts, sodium nitrate, and ammonium sulphate, heat 2 grams at 130° in an oil oven for 10 hours. The loss in weight is considered as moisture.

[As both of these recommendations involved changes in official methods, action on them was deferred until 1905.]

6. Phosphoric Acid.

It is recommended—

1. That the referee for next year plan field and pot experiments with cultivated plants, looking toward the establishing of the relative value of the total phosphoric-acid content of basic phosphate slags (both foreign and domestic), redonda and precipitated phosphates, of different degrees of fineness, in comparison with the phosphoric acid contained in acid phosphate and other common phosphatic materials found on sale in our markets, and invite cooperation on as many soil types and by as many workers as possible. [Adopted.]

2. That further study be made on the methods for determining total and available lime contained in basic phosphatic slags.

[After some discussion the recommendation was referred to the referee for 1905, with authority to act at his own discretion.]

3. That a study of the methods for determining total phosphoric acid in basic phosphatic slags be continued. [Adopted.]

4. That the referee for next year make a study of the solubility of the phosphoric acid in samples of the same slag, of different degrees of fineness.

[Referred to the referee for 1905, with authority to act at his own discretion.]

The report of Committee B on recommendations was next received.

REPORT OF COMMITTEE B ON RECOMMENDATIONS.

By C. A. Browne, Jr., *Chairman.*

(Dairy products, foods and feeding stuffs, sugar, and tannin.)

1. Sugar.

It is recommended—

1. Chemical methods: (a) That the sugar referee and his associate on chemical methods devote as much time as seems desirable during the coming year in cooperation with the committee of the International Commission for Unifying Methods of Sugar Analysis having in charge the revision of reducing sugar methods, for the purpose of obtaining more satisfactory and more uniform methods of determining reducing sugars. [Adopted.]

2. Special analytical methods: (a) That the methods for the determination of levulose and dextrose in the presence of sucrose be given further trial;

(b) That the study of methods for the identification and analysis of the vegetable gums be continued; and

(c) That some effort be made toward perfecting methods for the determination of caramel and the other organic solids which accompany sugar in cane and beet products. [Adopted.]

3. Molasses analysis: (a) That the association consider the adoption of the neutral oxalate of potassium in place of sodium carbonate as a precipitant for lead from clarified sugar solutions which are to be tested for reducing sugars. It has been known for several years that an excess of sodium carbonate redissolves a portion of the lead precipitate in the presence of invert sugar. It has been found by the associate referee that potassium oxalate does not behave in this objectionable manner, and, so far as he has been able to ascertain, there is no drawback to its use.

It is not recommended that the present method be changed this year, but it is suggested that the referee on sugar for the next year be requested to test this new precipitant.

[Referred to the referee for 1905, with instructions to act at his own discretion.]

(b) That the referee on sugar, or one of his associates, be requested to submit to collaborative test next year the methods of molasses analysis outlined at the meeting in 1903.[a] [Adopted.]

2. Tannin.

It is recommended—

1. That further research be made with the object of establishing a limit of temperature at which the determination of soluble solids and insolubles shall be conducted. [Adopted.]

2. That the method for analysis of barks, woods, etc., as set forth in the referee's report, be printed as a provisional method, and trials continued until it has been perfected. (See p. 199.) [Adopted.]

3. That the method for the determination of acid in tannin solutions, with the alternative of using the cold charcoal method, be continued as a provisional method and given further study. [Adopted.]

4. That the referee for 1905 make a study of present methods of analysis of tannery-yard liquors, especially spent or "sapped" liquors. [Adopted.]

5. That the recommendations submitted in the report for 1903 be embodied in the official (?) method.

These changes read as follows:

1. That the last sentence of paragraph II, Quantity of material (Bul. 46, Methods of Analysis, p. 79), be changed to read as follows:

"In case of extracts, weigh in a weighing bottle fitted with a ground-glass stopper such quantity," etc.

2. That the last sentence of paragraph V, Soluble solids (Bul. 46, Methods of Analysis, p. 80), be changed to read as follows:

"That the funnel shall be covered with a plate during filtration, and all other means be taken to guard against evaporation."

[A discussion followed as to whether these methods on tannin, as given in Bulletin No. 46, were official or not, and the secretary was empowered to determine this point and adopt these changes, officially or provisionally, in accordance with the facts. By reference to Bulletin No. 73, Proceedings of the nineteenth annual convention, footnotes on pages 174 and 175, it will be seen that the same question was raised, and subsequent investigation showed that the tannin methods *had never been adopted as official.* A circular letter addressed to the executive committee procured permission to insert the word "provisional" over the methods on tannin in Bulletin No. 46 when revised.

Accordingly the above recommendations are adopted as changes in the provisional method appearing in Bulletin No. 46.]

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[a] U. S. Dept. Agr., Bureau of Chemistry, Bul. 81, p. 175.

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3. Foods and Feeding Stuffs.

[As no work was done on this subject in 1903 the recommendations for the preceding year were again referred to the referee for 1904–5.]

It is recommended—

1. That the referee be requested to study the composition of the ether extract obtained after digesting with pepsin the residue obtained by the official method of fat extraction.

2. That the modified König method for the determination of crude fiber be further investigated, especially to ascertain whether the glycerol-acid mixture hydrolyzes any of the true fiber.

4. Dairy Products.

It is recommended—

1. That the two lines of work of this year be continued for another year.

2. That the referee be requested to study the methods for determining sugars in condensed milk and milk powders, or dried milks.

The report of Committee C on recommendations was then presented by the chairman:

REPORT OF COMMITTEE C ON RECOMMENDATIONS.

W. D. Bigelow, *Chairman.*

(Food adulteration.)

1. Baking Powder and Baking Chemicals.

It is recommended—

1. That the Wolff method for the detection of tartaric acid and tartrates and the silver mirror test, after shaking sample with 10 per cent ammonia-water and filtering (see Brooks on the Rapid Analysis of Cream of Tartar and Tartaric Acid Baking Powders, J. Amer. Chem. Soc., 1904, *28:* 813) be further studied. [Adopted.]

2. Tea and Coffee.

It is recommended—

That the methods outlined by the referee on tea and coffee be adopted provisionally. (See p. 38.) [Adopted.]

3. Beer.

It is recommended—

That the changes in methods and the new methods recommended by the referee on beer be printed in the Proceedings and further studied. (See p. 65.) [Adopted.]

4. Distilled Liquors.

It is recommended—

1. That the association consider the substitution of the alcohol tables given in the Gaugers' Manual of the Bureau of Internal Revenue, Treasury Department, for the alcohol tables of the association. [Adopted.]

2. That the Amthor test for caramel, as modified for distilled liquors by Lasché, be adopted as provisional. (Add 10 cc of paraldehyde to 5 cc of the sample contained in a test tube and shake. Then add absolute alcohol, a few drops at a time, shaking after each addition until the mixture becomes clear. Allow to stand. Turbidity (after ten minutes) is indication of caramel. The Brewer Distiller, May, 1903.) [Adopted.]

3. That the referee make a critical study of the additional methods suggested by the collaborating analysts this year for the presence of artificial coloring matter, and other tests to distinguish adulterated liquors. (See p. 31.) [Adopted.]

4. That the referee make a further study of methods for the estimation of fusel oil. [Adopted.]

5. Preservatives.

It is recommended—

1. That Method B, page 108, of Bulletin 65,[a] for the determination of formaldehyde be discontinued. [Adopted.]

2. That methods Nos. 5, 6, and 7 (2), pp. 47–49, for determining formaldehyde, be given further trial by the association; as well as the Jorissen method, as given on p. 64. [Adopted.]

6. The Separation of Vegetable Proteids.

It is recommended—

1. That for the present no attempt be made by Methods A, B, and C to separate the proteids of wheat into individuals, and that only such names be applied as describe the process of separation, viz, (a) proteids soluble in alcohol; (b) proteids insoluble in alcohol; (c) proteids soluble in dilute salt solution. [Adopted.]

2. That Methods A, B, and C, for the separation of the proteids of wheat, as given in the referee's report (p. 125), be used provisionally. [Adopted.]

3. That further tests as to the overlapping of the different proteids be made. [Adopted.]

7. Separation of Meat Proteids.

It is recommended—

That the methods given by the referee for the determination of ammonia, chlorin, and phosphoric acid be adopted as provisional, and the method suggested for the determination of xanthin bases be further studied. (See p. 129.) [Adopted.]

At the close of the reports of the committees on recommendations Mr. Huston extended to the association an invitation from the Association of American Fertilizer Manufacturers to hold a joint meeting on Wednesday morning at 10 o'clock. Doctor Wiley spoke on the value of cooperation with the association named, and on motion the invitation was accepted.

The committee on resolutions then made its report.

REPORT OF COMMITTEE ON RESOLUTIONS.

Whereas the methods employed by the Association of Official Agricultural Chemists for the analysis of soils and those employed by the Bureau of Soils of the United States Department of Agriculture yield such entirely different results where they should be identical,

Resolved, That a committee be appointed to consider the matter and to consult with the Secretary of Agriculture with a view to bringing about greater harmony in respect to methods employed in soil analysis in the United States and the conclusions based upon such analyses.

L. L. Van Slyke,
Harry Snyder,
G. S. Fraps,
Committee on Resolutions.

The resolution was carried, and the chairman appointed the following committee: L. L. Van Slyke, chairman; H. J. Wheeler, and F. K. Cameron.

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[a] Provisional methods for the analysis of foods, Bureau of Chemistry, Department of Agriculture.

The report of the committee on nominations was then presented as follows:

REPORT OF COMMITTEE ON NOMINATIONS.

For president, Mr. C. L. Penny, of Delaware; for vice-president, Mr. C. G. Hopkins, of Illinois; for secretary, Mr. H. W. Wiley, of Washington, D. C.; as additional members of the executive committee, Mr. C. A. Browne, jr., of Louisiana, and Mr. R. W. Thatcher, of Washington.

B. B. Ross.
A. E. Leach.
R. J. Davidson.

The report of the committee was unanimously adopted, and the officers named were declared elected for the year 1904–5.

The committee on amendments made no report, and the standing committees were then declared in order.

The report of the chairman of the food standards committee was presented by the secretary in Mr. Frear's behalf.

REPORT OF COMMITTEE ON FOOD STANDARDS.

Mr. President and Members of the Association: On behalf of the pure food standards committee I desire to make the following report of progress:

Since the last meeting of the association the committee has met once, May 12–19, in New York City. This meeting was especially devoted to receiving the suggestions of manufacturers and others with respect to the standards for articles not included in the schedules proclaimed November 20, 1903. Notice of the meeting had been earlier given by circular letter to organizations, firms, and food control officials and by publication in trade journals. At these sessions appeared, among others, representatives of the United States Sugar Refining Company, urging the insertion in the sugar schedule of a separate definition and standard for "refiner's sirup;" A. S. Hoyt, of A. S. Hoyt & Co., respecting standard for gluten flour; A. W. Duckwall, bacteriologist of the Canners' Association, respecting the uses of preservatives in catchups, etc.; representatives of the Association of Manufacturers and Distributers of Food Products, respecting the definitions and standards for preserves and jellies; representatives of the H. J. Heinz Co., respecting the use of preservatives in catchups and preserves, and respecting vinegar standards; with reference to fruit juices and wines, representatives of the Italian Chamber of Commerce of New York City, of the Gleason Grape Juice Company, and of the Urbana Wine Company; representatives of the Fruit Dealers' Association of New York, respecting a standard for evaporated fruit; a representative of the Tea Association of New York City, respecting tea standards; representatives of the American Baking Powder Association and of the Royal Baking Powder Company, respecting the practicability of a standard for baking powders; respecting the general subject of the uses of preservatives and coloring matters in foods, representatives of H. Kohnstamm & Co., H. Lieber & Co., and the Preservaline Manufacturing Company, also Dr. R. G. Eccles, of Brooklyn; with reference to olive oil, representatives of the Italian Chamber of Commerce, and Maj. W. H. Thomas, of Louisville, Ky., respecting whisky standards.

The committee has also prepared for publication at an early date tentative standards for articles belonging to the schedules of cereals and their milling products; fruits, evaporated and preserved; honey, salad oils, vinegar, and fruit juices, fresh and fermented. These will be distributed for criticism preparatory to their recommendation for final adoption.

At the request of your committee, the Bureau of Chemistry has undertaken comprehensive investigations of American meat extracts and of maple sugar products to guide in the work of fixing standards for these products. Upon the latter subject Mr. Julius Hortvet, chemist to the Minnesota Dairy and Food Commission, is also rendering highly valuable aid.

Respectfully submitted.

WM. FREAR, *Chairman.*

The report was approved and the committee continued. The report on fertilizer legislation was then presented by the chairman of that committee.

REPORT OF COMMITTEE ON FERTILIZER LEGISLATION.

Your committee has considered further the propriety of attempting to secure an enactment by the Congress of the United States of a law regulating interstate commerce in fertilizing materials and fertilizers. The attention of this body has often been called to the desirability of such legislation. At the present time nearly all the States of our Union have laws regulating the manufacture and sale of fertilizers and fertilizing materials within their borders. These laws differ from each other in many particulars and especially in respect of those for labeling and tagging the packages intended for sale within their respective boundaries. The result of this multiplicity of regulations is to throw a great, and it seems to us largely unnecessary, burden upon the manufacturers. It appears to your committee that one of the most desirable results which would follow the enactment of an interstate fertilizer law would be the tendency which it would have to bring State legislation into harmony therewith. There would be, evidently, a gradual approach in the State laws to the standards and regulations of the national law. In illustration of this it may be said that although there is no national law regulating interstate commerce in food products, yet the fact that bills proposing to regulate interstate commerce in such products have been constantly before Congress for the past 15 years has influenced in a marked degree the State legislation. Many of the State laws very closely approximate to the conditions prescribed by the proposed national legislation. If this salutary effect is produced by a proposed measure, might we not reasonably expect that the effect of an enactment of such a bill into a law would produce still more marked results? Your committee, therefore, believes that it would be advisable for this association to prepare, carefully and judiciously, a measure which should be introduced into the Congress of the United States providing for the regulation of interstate commerce in fertilizers and fertilizing materials, and empowering the Secretary of Agriculture, with the assistance of this association and trade and other experts, to prepare and promulgate standards for the materials in question.

Here, again, we may refer to what has been accomplished in the way of foods: The Congress of the United States has authorized the Secretary of Agriculture to promulgate food standards, or standards of purity for food products, and has authorized him to collaborate with this association and other trade and technical experts in reaching a just decision in regard to what these standards should be. Great progress has already been made in this direction, and, we may say, with entire satisfaction not only to the scientific but also to the commercial world. The establishment of such standards tends to remove the cause of discontent, disagreement, and litigation, which so often is due solely to a lack of an authoritative definition of standards. Your committee believes that a similar process in the case of fertilizers and fertilizing materials would produce equally salutary results.

It is evident that any measure of this kind should be formulated with the greatest care and should be submitted to this association for general discussion before it is offered as a bill in the Congress of the United States. It should also be submitted

to the manufacturing industries and those engaged in the transportation of fertilizers and fertilizing materials in order that the interests of all parties concerned may be conserved.

It is evident that great care should be given to the definitions which such a measure should contain. In order that your committee may make a tentative step in this direction the following brief outline of definitions and adulterations may be offered for consideration:

DEFINITIONS.

SEC. —. That the term "fertilizer" as used in this act shall include all substances intended for application to the soil to increase the fertility thereof, save as hereinafter excepted. The term "fertilizer ingredient" shall include all substances intended to be used directly as fertilizers or in the composition thereof, provided that dung and all forms of barnyard manure, sewage, human excrement or the excrement of other animals in the crude or unmanufactured state, land plaster or gypsum, and common salt shall be excepted from the provisions of this act.

ADULTERATIONS.

SEC. —. That for the purposes of this act an article shall be deemed to be adulterated in case of fertilizers and fertilizer ingredients if any valuable ingredient thereof has been extracted or replaced by a less valuable or an inert ingredient.

SEC. —. That for the purposes of this act an article shall be deemed to be misbranded—

First. If any false name or property be ascribed to any ingredient either in the label or in the guaranty of the vender.

Second. If any valuable ingredient be present in less quantity than claimed on the label or in the guaranty of the vender.

Third. If any valuable ingredient be present in a form different from that named in the label or guaranty of the vender.

Fourth. If any property or quality be ascribed to the article as a whole not warranted by the composition thereof.

The above are not submitted for the purpose of adoption or for any final action, but simply to indicate in a general way some of the points which should be considered in the formulation of a bill for presentation to the National Congress.

Your committee respectfully submits the above as a report of the progress made during the preceding year and asks that the committee be continued and authorized specifically to take steps looking to the preparation of a bill regulating interstate traffic in fertilizers and fertilizing materials, to be presented to the Congress of the United States after approval by this association.

We have the honor to be

Very respectfully,

H. W. WILEY, *Chairman.*
B. W. KILGORE.
H. B. MCDONNELL.
H. A. HUSTON.
B. B. ROSS.

In connection with this report it is desired to submit in part a letter received from the California station on this subject:

BERKELEY, CAL., *September 19, 1904.*

DR. H. W. WILEY,
Chairman Committee on Fertilizer Legislation,
Association of Official Agricultural Chemists.

DEAR SIR: We have just received the Proceedings of the Twentieth Annual Convention, Association of Official Agricultural Chemists, and have seen for the first time just what was done regarding Federal fertilizer legislation and uniform State

legislation on the same subject. We see that the committee on fertilizer legislation was instructed to confer with manufacturers and distributers and other persons interested and report at the next meeting the form that national legislation should take, etc. California having enacted a fertilizer law which went into effect July 1, 1903, we are interested in the question and beg to be heard upon it.

We believe that uniform legislation is highly desirable, almost a necessity; but we should dislike very much to see the enactment of a Federal law, or recommendations from the Association of Official Agricultural Chemists for uniform State laws that did not embrace everything essential to good control work. We should dislike to see this for two reasons: First, a Federal law once passed, or recommendations for uniform State laws finally agreed upon, it would, to say the least, be a long period before they would be improved upon. Second, we have in this State what we consider a highly satisfactory law, and we should dislike very much to see anything recommended or enacted which would fall short of its provisions. Although it might not be obligatory upon the States to enact such uniform provisions recommended, if a majority or nearly all of the States should enact laws which do not require as much information of the manufacturers as does the California law it would be a very strong lever for manufacturers to use upon the legislature for the repeal of certain of its provisions.

Under the California law the manufacturer is required to state the percentage of each ingredient present in its *various forms* and also the materials from which the ingredients are derived. The inclosed registration blank will indicate to you the form of guaranty which the manufacturer is required to submit before he receives his registration certificate, and this information is required upon the tags accompanying the bags.

The guaranty is, of course, the essential part of a label; and we can see no reason why the manufacturer should not be required to state fully the composition of the fertilizer. It may be that the minor details of execution of the California law may be improved upon, but we do believe that we have succeeded, after a long, hard struggle, in enacting a law that in its essentials can not be surpassed, and, if we are not mistaken, it has gone a step further than any other law in that it requires a quantitative statement of various forms in which the ingredients are present. Hence we are solicitous lest anything should be done which might in any way jeopardize the good effects of our law.

The feature of the law above referred to may not appeal to the Eastern farmer as much as it does to the farmer in our arid region. He realizes that the form and quantity of fertilizing materials which he is using should be matters of exact information with him, and a large majority of our farmers intelligently study these questions. * * *

We note with surprise the statement made as to the ignorance of farmers[a] that they are unable to understand the difference between soluble, available, and total phosphoric acid, even though the same is explained fully in bulletins accessible to everyone. The simplicity of guaranties which is advocated by the State chemist of Maryland and which is also emphasized in the law, as given by State Chemist Kilgore, of North Carolina,[a] proposed by the Cotton States Association of Commissioners of Agriculture, we consider would be a serious retrograde step. * * * If the farmer does not know how to distinguish between the agricultural signification of legumes on the one hand and true grasses on the other, because in the past the name "grasses" has been applied to forage plants at large, it is high time such distinctions should be made plain to him in order that he may be able to avail himself of the progress of agricultural science. * * * We wholly dissent from the doctrine that because things are now in an unsatisfactory condition they should be allowed to remain so indefinitely by the action of those whose moral and legal duty is to promote a better state of affairs. * * *

Very truly, yours,

E. W. Hilgard,
Director.

Geo. Roberts,
Assistant Chemist in Charge of Fertilizer Control.

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[a] U. S. Dept. of Agriculture, Bureau of Chemistry, Bul. No. 81, pp. 210 and 207.

APPLICATION TO THE REGENTS OF THE UNIVERSITY OF CALIFORNIA FOR LICENSE TO SELL FERTILIZERS.

[In accordance with the act of the legislature of California "To regulate the sale of commercial fertilizers."]

I, ——— ———, a citizen of ———, county of ———, State of ———, do hereby certify that I am ——— (official title) of the firm or corporation of ——— ———, (address), manufacturers of fertilizers, and as such am authorized to make this affidavit, and that the following brands of fertilizers, which said manufacturers propose to offer and expose for sale in the State of California during the year ending June 30, 190–, are guaranteed by said manufacturers to contain the minimum percentages of essential ingredients stated below, derived from the sources stated:

Name, brand, or trade-mark of fertilizer.	Guaranteed minimum analysis, per cent, and sources.											
	Phosphoric acid.				Nitrogen.					Potash.		
	Available.	Insoluble.	Total.	Derived from.	Nitric.	In ammonia salts.	Organic.	Derived from.	Total.	Muriate.	Sulphate.	Total.

Given under my hand, this —— day of ———, 190–.

(Signature of affiant) ——— ———.

STATE OF ———, *County of* ———, *ss.*

On this —— day of ———, in the year 190–, before me, a notary public in and for said ——— County, residing therein, duly commissioned and sworn, personally appeared ——— ———, known to me to be the person whose name is signed to the foregoing statement, and made oath that said statement is true and correct and that he executed the same.

In witness whereof I have hereunto set my hand and affixed my official seal, at my office, in the county and State aforesaid, the day and the year in this certificate first above written.

———— ————,

Notary Public in and for County of ———, *State of* ———.

Mr. WILEY. I wish to submit to the association a statement made by Mr. McDonnell, of the Maryland station, in regard to the conversion tables prepared by him, on which there was some discussion at the last meeting, their publication in the Proceedings having been considered. Mr. McDonnell says:

I have published a revised edition of the tables, with the approval of the other members of the committee, and shall be glad to furnish copies of them, free of charge, as long as the supply lasts. I think it would now be unnecessary to print the tables in the Proceedings, but will be glad to furnish the plates if this is desired.

I think that this is a very satisfactory arrangement, as the constants of nature involved are constantly changing, and it seems unwise to reprint the tables in the Proceedings, which are already very bulky. The report containing these tables is the Maryland Agricultural Quarterly, Supplement to No. 24, May, 1904, Conversion tables for calculating fertilizer and feed-stuff analyses, second edition, revised.

Before adjournment I wish to speak of the two members of this association who have been removed by death since we last met—Mr. E. E. Ewell, who died on February 7 last, and Mr. Norman Robinson, who died on February 4. I move that as a mark of respect for our deceased associates we rise in our places for a few moments.

The members of the association rose and stood with bowed heads.

The association having completed its program the meeting adjourned sine die, with the understanding that the members would attend the meeting of the Fertilizer Manufacturers' Association, in accordance with their invitation, at 10 o'clock the following day, in the agricultural building.

THIRD DAY.

WEDNESDAY—MORNING SESSION.

At the opening of the second day of the meeting of the Fertilizer Manufacturers' Association at half-past ten in Room Q of the Agricultural Building, President C. H. MacDowell extended a hearty greeting to the chemists present, expressing his appreciation of the extent to which they, as an association, were dependent on the chemist's work, and then called on Acting President Withers, of the Association of Official Agricultural Chemists, who spoke briefly as follows:

REMARKS OF MR. W. A. WITHERS.

Mr. President: In behalf of the Association of Official Agricultural Chemists, of which I have the honor to be acting president, I wish to thank the Association of American Fertilizer Manufacturers for the kind invitation to us to join with them in this meeting. The fertilizer manufacturers and agricultural chemists are both interested in fertilizers, but consider the subject from different standpoints. The aim of the work of each, like that of the practical farmer, is "to make two blades of grass grow where only one grew before."

When the first experiment station of the world was established at Moeckern, a little over 50 years ago, its principal work was the analysis of commercial fertilizers for the mutual benefit of the farmer and manufacturer. Similarly, when the first experiment station was established in the United States its principal work was to analyze commercial fertilizers. During our lifetime, and perhaps for many years afterwards, the trade work will constitute an important part of the labors of the agricultural chemist. But as the scope of experiment station work has been extended to include not only chemical work, but a study of plant breeding, plant diseases, animal feeding, etc., so the work of the agricultural chemist has been broadened, and his work now includes not only the analysis of fertilizers for the trade, for the fertilizer control, and for the farmer himself, but in many cases he cultivates experimental plots and analyzes the soil, crop, and fertilizers in connection with them, with the view of ascertaining the fertilizing elements best adapted to different plants in different localities.

Our association has just attained its majority, but it has already far outgrown its original scope, and now includes a study of methods for the determination of the composition of all agricultural products and of the substances which contribute to the growth of plants and animals.

The work of these two organizations is therefore closely allied. We are interested in hearing what you have to say, and I wish again, in behalf of my associates, to thank you for your invitation to be present at this meeting.

Mr. Wiley, as secretary of the Association of Official Agricultural Chemists and chairman of the committee on fertilizer legislation, then addressed the meeting as follows:

ADDRESS ON THE RATIONAL USE OF FERTILIZERS.

By H. W. Wiley.

As chairman of the committee of the Association of Official Agricultural Chemists on legislation relating to fertilizers I am more than glad of the opportunity of meeting the representatives of the fertilizer manufacturing trade. In the report which I made at our meeting yesterday, as chairman of that committee, I referred to the desirability of collaboration between our association and yourselves in the preparation of a proper measure to be introduced into the National Congress. Perhaps I might be permitted to read that portion of the report relating to the necessity of this collaboration. (See p. 229.)

What the vote would be on such a law if introduced in the National Congress we can only prophesy. However, if the memberships of our two organizations are united, if all the interests which are engaged in these industries could be harmonized and a measure agreed upon, there can be no doubt that this influence toward the passage of such a law would be felt. If, however, any interests represented in large investments of agricultural properties should combat the proposed measure and use influence to prevent its culmination into a law, it would certainly delay any action thereon. It seems to me, as the acting president of our association has said, that while the chemist and manufacturer may look at the subject of fertilizers from a different point of view, there can scarcely be any difference of opinion in regard to the fundamental features which should control national legislation. Such a law should not be framed as discrimination in favor of one industry against another, but should look to the interests of all the industries involved because their prosperity must depend upon mutual interests and mutual help or their depression be due to adverse criticism. What is to the best interest of the farmer and agricultural chemist must also be to the best interest of the manufacturer. If your goods are not available to the farmer you would be unable to find a market for them, and if for any reason the agricultural industry should turn against your product you would be compelled to go out of business. Therefore it becomes a trade necessity for you to supply the materials which the farmer wants, and, on the other hand, it becomes an agricultural necessity for the farmer to use those materials in a proper manner. While we as agricultural chemists teach the farmer the proper manner of using plant foods and the most economical manner of using them to get the best results, it becomes the duty of the manufacturer to produce foods of a character required to produce these results.

There is a very widespread belief that the magnitude of a crop, other things being equal, depends upon the amount of plant food at its disposal. Just as the farmer in feeding an animal would feed him for a definite purpose, so the farmer of a scientific turn of mind would feed his crop for a definite purpose. The man who grows sugar cane in Louisiana feeds his crop to produce sugar; the man who grows sugar beets in Colorado feeds the crop for the purpose of producing sugar; the man who grows wheat feeds his crop for the purpose of producing grain which contains the proper amount of protein and other ingredients for milling and baking purposes, and the man who raises Indian corn will feed it for improving the oil content, the protein content, or the starch content, according to the purpose for which the grain is to be used. As you know, the starch made in the United States is made almost exclusively of Indian corn. Therefore it would be proper and thoroughly scientific for the farmer who grows Indian corn for the purpose of producing starch to so feed it as to make

as much as possible of that element in the corn. The same would hold true should he be desirous of growing corn for the protein or oil content. On the other hand, if he should use his Indian corn for feeding working animals he would probably desire less starch and more protein in his corn, and if he wishes to use it for feeding the human animal the same would be true. So the character of a crop may be, to a large extent, determined by the kind of food that it is given. Now, the man developing a race horse for the purpose of running a race who would feed it as he feeds his coach horse would be committing sporting suicide, because he would be putting the animal in a condition in which it would be impossible for it to win a race. He would feed the animal to keep it lean and muscular, and not care so much about the development of fat and sleekness. And so the crop must be fed in the same scientific way.

Now, if nature had stored in the soil inexhaustible supplies of plant food in a shape in which it could be utilized by the crop, your services would not be necessary; but experience has shown that no matter how rich a virgin soil may be, if subjected to continual cropping for agricultural purposes the fertility of that soil diminishes, and in order that it may be maintained or restored to its original degree of fertility the application of fertilizers must be made. Hence the necessity of collecting from these natural deposits, which you have mentioned, the plant foods there stored and bringing them to a point where they can be immediately available for crop use.

Statistics give us some interesting facts regarding agricultural results in different parts of our country. I do not want to say anything to offend our Southern friends, but they must acknowledge that the soils which have been long under cultivation, like those of North and South Carolina, for instance, have been reduced to a low state of fertility, and therefore, to produce a crop, they require more fertilizing materials than soils in the West. A comparison, for instance, of the soils of Illinois and the soils of Georgia would show how superior the former are for growing a crop, and if you could transport the State of Illinois into Georgia, taking 18 inches of its surface, you would grow larger and better crops in Georgia without a pound of fertilizer than you can now in that State with their abundant use. But the time will come when the soil fertility of Illinois will be diminished to such an extent that it will not produce such large crops. Scientific agriculture demands a knowledge on the part of the farmer of the plant foods in the soil, and, where there is a lack of fertility, that it may be restored as nearly as possible to the original condition of the soil. Any system of agriculture which does not preserve the fertility of the soil and increase it when low is not a scientific system of agriculture.

In the great wheat fields of north France, at the the present time, they have an average yield of wheat of 27 bushels per acre, whereas 50 years ago they had only 17. The average yield of wheat in England is over 33 bushels per acre, and that yield is secured by heavy fertilization and by scientific rotation of crops and cultivation; and if the English farmer should allow his soil to become so reduced in fertility as to grow only 13 bushels per acre, which is the average yearly production in this country, he would soon become bankrupt. What I have said about wheat is true of all other crops. We do not need more acres of wheat. We want to raise our 13 bushels per acre to 27 or even more than that. These gentlemen who are here from the experiment stations know that such yields can be secured by systematic, scientific agriculture. At the experiment station in Maryland, on land which a few years ago would not produce 7 bushels of wheat per acre, they now raise crops of from 30 to 40 bushels per acre every year on a worn-out soil, which shows what a scientific system of agriculture and judicious fertilization may accomplish on soils which have been exhausted. If we would take our Indian corn crop, which is raised over an area of 100 million acres in this country, with an average yield of 27 bushels per acre, and cut that down to 50 million acres and raise the yield to 54 bushels per acre, we would have just as much Indian corn as we have to-day and a much more

remunerative return to the farmer. We have not much more land to give to Indian corn nor to wheat until the great regions of the West, which are now in process of irrigation, are recovered, and therefore the progress of American agriculture is to be effected by increasing the yield and not by extending the acreage of the crop. So by the collaboration of the agricultural chemists and the manufacturer of fertilizer the scientific farmer will be able, I believe, within the next 50 years, to increase the yield of our staple crops to at least double what they are to-day, and that, too, without increasing the acreage under cultivation. To this end let us all work heartily together.

The following papers were then read and may be found in full in the American Fertilizer for October, 1904:[a]

The Present Condition and Outlook of the Phosphate Industry in Tennessee, by Lucius P. Brown; Pyrites, by Otto Mayer; Fertilizers from the Farmer's Standpoint, by Herbert Myrick.

After the reading of these papers the meeting adjourned.

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[a] Vol. 21, No. 4, published in Philadelphia.

OFFICERS, REFEREES, AND COMMITTEES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR 1905.

President.

Mr. C. L. Penny, Newark, Del.

Vice-President.

Mr. C. G. Hopkins, Urbana, Ill.

Secretary.

Mr. H. W. Wiley, Washington, D. C.

Additional members of Executive Committee.

Mr. C. A. Browne, Jr., New Orleans, La.
Mr. R. W. Thatcher, Pullman, Wash.

Referees.

Phosphoric acid: E. W. Magruder, Richmond, Va.
Nitrogen:
Determination of nitrogen: Floyd W. Robison, Lansing, Mich.
Separation of nitrogenous bodies: R. Harcourt, Guelph, Canada (milk and cheese proteids).
Potash: G. S. Fraps, College Station, Tex.
Soils: C. G. Hopkins, Urbana, Ill.
Dairy products: G. E. Patrick, Washington, D. C.
Foods and feeding stuffs: J. O. LaBach, Lexington, Ky.
Food adulteration: W. D. Bigelow, Washington, D. C.
Sugar: L. S. Munson, Washington, D. C.
Tannin: H. C. Reed, Stamford, Conn.
Insecticides: B. H. Smith, Washington, D. C.
Inorganic plant constituents: R. W. Thatcher, Pullman, Wash.
Medicinal plants and drugs: L. F. Kebler, Washington, D. C.

Associate Referees.

Phosphoric acid: J. A. Bizzell, Ithaca, N. Y.
Nitrogen:
Determination of nitrogen: J. H. Gibboney, Blacksburg, Va.
Separation of nitrogenous bodies:
Meat proteids: W. D. Bigelow, Washington. D. C.
Vegetable proteids: J. S. Chamberlain, Washington, D. C.
Potash: A. L. Knisely, Corvallis, Oreg.
Soils: R. H. Loughridge, Berkeley, Cal.
Dairy products: F. W. Woll, Madison, Wis.
Foods and feeding stuffs: J. K. Haywood, Washington, D. C.

Food adulteration:

(1) Colors: W. G. Berry, Appraiser's Office, New York, N. Y.
(2) Saccharine products, including confectionery: J. Hortvet, St. Paul, Minn.
(3) Fruit products: E. M. Bailey, New Haven, Conn.
(4) Wine: G. E. Colby, Berkeley, Cal.
(5) Beer: H. E. Barnard, Concord, N. H.
(6) Distilled liquors: C. A. Crampton, Washington, D. C.
(7) Vinegar: Richard Fischer, Madison, Wis.
(8) Flavoring extracts: E. M. Chace, Washington, D. C.
(9) Spices: A. L. Winton, New Haven, Conn.
(10) Baking powder and baking chemicals: R. O. Brooks, Trenton, N. J.
(11) Meat and fish: M. E. Jaffa, Berkeley, Cal.
(12) Fats and oils: L. M. Tolman, Washington, D. C.
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(14) Cereal products: A. McGill, Ottawa, Canada.
(15) Infants and invalids' foods: H. W. Wiley, Washington, D. C.
(16) Vegetables: W. N. Berkeley, San Juan, P. R.
(17) Condiments other than spices: J. D. Hird, Washington, D. C.
(18) Cocoa and cocoa products: E. N. Eaton, Chicago, Ill.
(19) Tea and coffee: H. C. Lythgoe, Boston, Mass.
(20) Preservatives: W. D. Bigelow, Washington, D. C.

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Molasses methods: H. E. Sawyer, Boston, Mass.
Special analytical methods: C. A. Browne, jr., Audubon Park, La.

Tannin: F. P. Veitch, Washington, D. C.
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CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of the United States. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State or national agricultural experiment station or agricultural college, or with any State or national institution or body charged with official control of the materials named in section 1, shall alone be eligible to membership; and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers. All persons eligible to membership shall become members ex officiis and shall be allowed the privileges of membership at any meeting of the association after presenting proper credentials. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice-president, and a secretary, who shall also act as treasurer; and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the executive committee, at the regular annual meeting, a referee and such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate.

It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of analysis used in official inspection, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of the particular inspection affected to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

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